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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. - Publisher.

THE CHEMISTRY OF COMPOUNDS OF VARIABLE COMPOSITION

IV. THE TANTALUM-SELENIUM SYSTEM

S. M. Ariya, A. I. Zaslavsky and I. I. Matveeva

We investigated the tantalum-selenium system, which is not described in the literature, to establish the lengths of regions of homogeneity, which have compounds in them.

Tantalum selenide preparations were made by sintering metallic tantalum with selenium. Tantalum foil, containing an insignificant amount of niobium, was carefully hydrogenated with pure hydrogen; the friable tantalum hydride formed was ground to powder which was then freed from hydrogen by heating in vacuum at 900°. Analytical-grade selenium was twice distilled in vacuum for additional purification. The Ta-Se mixtures were gradually heated up to 900° in quartz ampules, evacuated to high vacuum. In most cases, after long sintering the samples were carefully ground and again heated at 900° for two days. Apparently, the preparations obtained in this way were completely homogeneous.

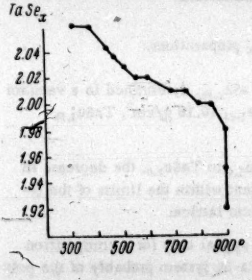

Fig. 1. The decomposition rate of tantalum selenide ($TaSe_{2.07}$) in vacuum. x = number of selenium atoms per atom of tantalum.

A preparation with a composition of $TaSe_{2.07}$ was heated in vacuum, increasing the temperature stepwise. It was heated for 4 hours at each temperature, after which the preparation was weighed. The results obtained are given in Fig. 1 which shows that the composition of the preparation practically corresponded to the formula $TaSe_{2.00}$ at a temperature close to 500°. Furthermore, the amount of selenium in the preparation practically did not decrease up to a temperature of 850°. Rather rapid decomposition of the selenide started at 900°. These data indicate that the composition $TaSe_{2.0}$ corresponds to some limit between phases.

We tried to determine the selenium vapor pressure over preparations of different composition at 900° using a gas flow method. Carefully purified argon was used as the carrier gas. It was found that the selenium vapor pressure rapidly decreased in approaching the composition $TaSe_{2.00}$, while with a selenium content less than in $TaSe_{2.00}$, it was very difficult to measure by the gas flow method. This forced us to carry out an x-ray investigation of the system Ta-Se.

X-radiograms of preparations with different composition were taken in a chamber of 57 mm diameter using copper radiation with a nickel filter. The x-radiograms are shown schematically in Fig. 2. The x-radiograms clearly show the presence of metallic tantalum and selenium in preparations in the composition range Ta-$TaSe_{1.0}$, while even at the composition $TaSe_{1.0}$ they contain no traces of metal. The same set of lines is found in x-radiograms for the range $TaSe_{1.0}$-$TaSe_{2.0}$, and furthermore, there is a hardly noticeable change in interplanar distances. The relative intensity of the lines, however, changes noticeably as can be seen, for example, by following lines 2 and 3 through the composition changes over this range. The diffraction picture changes, starting with a composition $TaSe_{2.1}$ and this is consistent with the results obtained on decomposing the selenide with the composition $TaSe_{2.07}$ in vacuum. Thus, it may be stated that tantalum selenide with a low selenium content has a region of homogeneity within the range $TaSe_{1.0}$-$TaSe_{2.0}$ (α-phase).

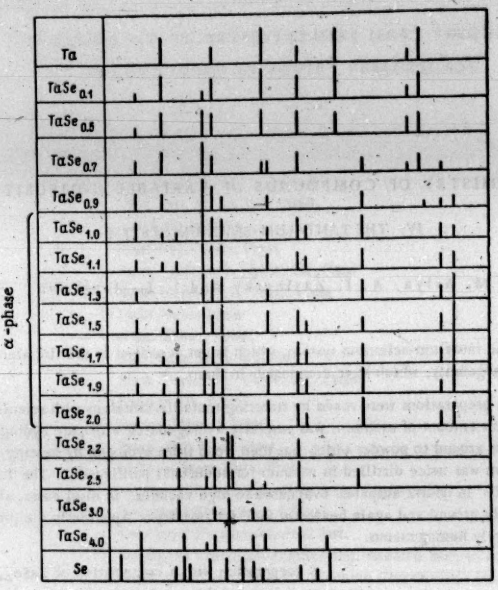

Fig. 2. Position of lines in powder x-radiograms of $TaSe_x$ preparations.

The density of preparations with compositions $TaSe_{1.04}$, $TaSe_{1.58}$ and $TaSe_{2.00}$, determined in a vacuum pycnometer at 20° with kerosene as the sealing liquid, were as follows: $TaSe_{1.04}$ 10.18 g/cm³, $TaSe_{1.58}$ 9.05 g/cm³, $TaSe_{2.00}$ 8.46 g/cm³.

As the lattice parameters change negligibly in the transition from $TaSe_{1.0}$ to $TaSe_{2.0}$, the decrease in density in this transition indicates that the relative increase of selenium content within the limits of the α-phase is due to the elimination of part of the tantalum atoms from the selenium lattice.

Free selenium lines are not detected for a composition $TaSe_3$ and they appear only for a composition $TaSe_4$. Apparently, besides the α-phase, even higher selenides exist in the Ta-Se system probably of the poly-compound type which are not the usual compounds of variable composition. The Ta-Se system thus appeared to be similar to the Ta-S system for which the following compounds are known: $TaS_{0.3}$-$TaS_{0.37}$ and $TaS_{1.0}$ - $TaS_{1.9}$ [1]. There is only one compound, WSe_2, in the system W-Se and its region of homogeneity is quite narrow ($WSe_{1.95}$-$WSe_{2.00}$) [2]; the transition from tantalum to tungsten is thus unusual in the sharp decrease in the region of homogeneity of the selenides. In subsidiary subgroups of the periodic table a tendency towards a decrease in length of the region of homogeneity of compounds is observed on moving down the subgroup. In connection with this, it is interesting to note that often the opposite takes place in the subsidiary sub-group of Group V. Three compounds were found in the V-Se system investigated over the range $VSe_{1.0}$-$VSe_{2.0}$: α-phase $VSe_{1.04}$-$VSe_{1.17}$, γ-phase $VSe_{1.62}$-$VSe_{1.97}$ and between them a β-phase [3]; the authors, apparently, were not sure whether the β-phase filled the complete composition range between the α- and γ-phases. Thus, the transition from the V-Se system to the Ta-Se system is characterized by an increase in the region of homogeneity. An analogous phenomenon was found recently by B. F. Ormont [4], when investigating vanadium and tantalum carbides.

SUMMARY

1. The existence of a compound in the region of homogeneity $TaSe_{1.0}$-$TaSe_{2.0}$ (α-phase) was established for the Ta-Se system. No compounds were found in the range Ta-$TaSe_{1.0}$. There are higher tantalum selenides besides the α-phase.

2. An increase in the relative selenium content in the α-phase is due mainly, and possibly exclusively, to the elimination of tantalum atoms from the lattice.

LITERATURE CITED

[1] Biltz and Kocher, Z. anorg. u. allgem. Chem. 238, 81 (1938).

[2] Glemser, Sauer and König, Z. anorg. u. allgem. Chem. 257, 241 (1948).

[3] Hoschek and Klemm, Z. anorg. u. allgem. Chem. 242, 49 (1938).

[4] B. F. Ormont, Theses of the Reports and Statements at the 3rd All-Union Conference on Physicochemical Analysis (Acad. Sci. USSR Press, 1955).

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THE LATTICE ENERGY OF SALTS WITH POLYATOMIC IONS

K. B. Yatsimirsky

It was previously shown [1] that with further refinement of A. F. Kapustinsky's equation [2] the lattice energy of ionic crystals could be calculated with an accuracy of ± 1-2 % for salts of the type MX, MX_2 and M_2X (with the exception of Na_2X).

The chemical bond is also extremely close to the ionic type in salts composed of an eight-electron ion (cation or anion) and a polyatomic or complex counter ion.

In 1947 we put forward a hypothesis [3] to the effect that a whole series of polyatomic anions could be characterized by completely determined effective radii, calculated from thermochemical data ("thermochemical radii"). Later, together with A. F. Kapustinsky [4], we gave additional grounds for such a hypothesis and showed the existence of a connection between the dimensions of the circumscribed sphere and the form of the ion, on the one hand, and its effective radius, on the other. It was also shown that the effective radii of polyatomic ions determine the magnitude of a whole series of other energetic properties of the ions [5].

In 1953 I. Sakamoto [6] carried out an extremely thorough caculation of the electrostatic component of the lattice energy (Coulombic attraction) for sulfates of barium, strontium and calcium. These values practically coincide with those calculated on the basis of effective radii. Here are the data:*

$BaSO_4$ 624.1 ± 4.8, 616 ± 12; $SrSO_4$ 647 ± 5.1, 644 ± 13; $CaSO_4$ 667.3 ± 7.5, 684 ± 14.

In connection with some modifications of A. F. Kapustinsky's Equation (1):

$$U = 287.2 \frac{\Sigma n Z_C Z_A}{r_C + r_A} \left[1 - \frac{0.345}{r_C + r_A} + 0.00870 (r_C + r_A) \right] \qquad (1)$$

it seemed interesting to use this quite accurate equation to recalculate the lattice energy and the heats of formation of gaseous polyatomic ions and then to check the agreement of the values obtained by this method.

The values for the lattice energy of salts with linear anions are given in Table 1. The effective radii of the ions: OH^-, HS^-, CN^-, CNO^- and CNS^- had been calculated earlier from thermodynamic data, the effective radius of HSe^- (r = 2.15 A) was calculated for the first time from thermodynamic data by the method of "differences" [5].

The derived values of the lattice energy of hydroxides and hydrosulfides for salts of the type MOH and MHS differ by 5-7 kcal from those calculated by Juza [7] and West [8] from crystallographic data.

The heats of formation of gaseous anions, given in Table 1, were calculated from the heats of formation of gaseous cations and solid salts taken from thermodynamic summaries [9] and our data [3]. The absence of considerable variations in the values of the heats of formation of gaseous ions indicates that the equation applied is sufficiently accurate. Some deviations in the cases of $Ca(OH)_2$ and $Sr(OH)_2$ (of the order of 4-5 Kcal) may be explained by the existence here of noticeable polarization.

*The first number is Sakamoto's figure, the second is ours.

TABLE 1

Lattice Energy of Salts with Linear Anions, and Heats of Formation of Some Gaseous Anions

Compound	$r_{OH^-} = 1.40$		$r_{HS^-} = 1.95$		$r_{HSe^-} = 2.15$		$r_{CN^-} = 1.82$		$r_{CNO^-} = 1.59$		$r_{CNS^-} = 1.95$	
	$U_{M(OH)_n}$	ΔH_{OH^-}	$U_{M(HS)_n}$	ΔH_{HS^-}	$U_{M(HSe)_n}$	ΔH_{HSe^-}	$U_{M(CN)_n}$	ΔH_{CN^-}	$U_{M(CNO)_n}$	ΔH_{CNO^-}	$U_{M(CNS)_n}$	ΔH_{CNS^-}
NaX	211.3	−36.7	178.0	−24.5	168.2	−5.6	184.8	17.3	198.4	−43.2	178.0	− 9.7
KX	188.7	−36.2	161.7	−24.6	153.7	−5.3	167.3	17.3	178.5	−43.1	161.7	−10.0
RbX	183.1	−34.1	155.2	−25.5	147.8	−6.0	160.5	—	170.6	—	155.2	−13.1
CsX	172.0	−35.3	149.3	−23.7	142.5	−4.3	154.1	—	163.3	—	149.3	—
CaX_2	617	(−41)	522	—	—	—	542	17	581	—	522	—
SrX_2	577	(−40)	493	—	—	—	511	—	545	—	493	—
BaX_2	549	−36	473	—	—	—	489	(24)	521	−42	473	—
Mean values		−36 ± 1		−24.6 ± 0.5		−5.3 ± 0.5		17 ± 1		−43 ± 1		−11 ± 2

TABLE 2

Lattice Energy of Salts with Nonlinear and Planar Singly Charged Anions, and Heats of Formation of Gaseous Anions

Compound	$r_{NO_3^-} = 1.55$		$r_{HCO_3^-} = 1.58$		$r_{CH_3CO_2^-} = 1.59$		$r_{HCO_2^-} = 1.63$		$r_{NO_2^-} = 1.89$	
	$U_{M(NO_3)_n}$	$\Delta H_{NO_3^-}$	$U_{M(HCO_3)_n}$	$\Delta H_{HCO_3^-}$	$U_{M(CH_3CO_2)_n}$	$\Delta H_{CH_3CO_2^-}$	$U_{M(HCO_2)_n}$	$\Delta H_{HCO_2^-}$	$U_{M(NO_2)_n}$	$\Delta H_{NO_2^-}$
NaX	200.6	−31.3	199.0	−102.0	198.4	−117.4	196.0	−176.5	181.1	−76.4
KX	180.6	−31.0	179.0	−102.1	178.5	−117.8	176.5	−175.9	164.2	−76.7
RbX	172.5	—	171.0	—	170.6	—	168.7	−178.1	157.6	−77.7
CsX	165.2	—	163.7	—	163.3	—	161.7	−176.8	151.1	−77.1
CaX_2	588	−27	468	−102	581	−119	574	—	531	−78
SrX_2	551	−28	432	−103	545	−120	539	—	501	−80
BaX_2	527	(−22)	400	−100	521	−115	515	—	480	−76
Mean values		−30 ± 2		−102 ± 1		−118 ± 1		−176.6 ± 0.6		−78 ± 1

TABLE 3

Lattice Energy of Salts with Polyatomic Anions and Heats of Formation of Gaseous Anions

Cations	$r_{ClO_4^-}$ = 2.00		$r_{ClO_3^-}$ = 2.36		$r_{MnO_4^-}$ = 2.40		$r_{CO_3^{2-}}$ = 1.85		$r_{SO_4^{2-}}$ = 2.30		$r_{CrO_4^{2-}}$ = 2.40	
	$U_{M(ClO_4)_M}$	$\Delta H_{ClO_4^-}$	$U_{M(ClO_3)_M}$	$\Delta H_{ClO_3^-}$	$U_{M(MnO_4)_M}$	$\Delta H_{MnO_4^-}$	$U_{M_MCO_3}$	$\Delta H_{CO_3^{2-}}$	$U_{M_MSO_4}$	$\Delta H_{SO_4^{2-}}$	$U_{M_MCrO_4}$	$\Delta H_{CrO_4^{2-}}$
Na^+	175.6	—56.2	159.3	—78.9	157.6	—	550	(—13)	485	(—138)	473	—137
K^+	159.7	—56.9	146.1	—80.6	144.7	—172.8	498	—22	445	—144	434	—142
Rb^+	153.3	—58.8	140.9	—81.3	139.6	—173.2	478	—28	429	—149	—	—
Cs^+	147.5	—56.9	135.9	—78.1	134.7	—172.7	459	—28	413	—145	—	—
Ca^{2+}	515	—	468	—	463	—	722	—48	634	—172	596	—198
Sr^{2+}	486	—57	445	—	441	—	675	—44	602	—171	—	—
Ba^{2+}	467	—55	429	—80	425	—	647	—40	579	—167	544	—195
Mean values		—57.4±1.1		—80 ± 1		—172.9±0.2		—35 ± 9		—157 ± 12		

The values for the lattice energies of salts with non-linear planar, pyramidal, and tetrahedral singly charged ions (NO_2^-, HCO_2^-, $CH_3CO_2^-$, HCO_3^-, NO_3^-, ClO_3^-, ClO_4^-, MnO_4^-) are given in Tables 2 and 3.

The heats of formation of the above gaseous anions were calculated from the heats of formation of crystalline salts [9, 3, 5] and of gaseous cations. The relatively small variations in the values obtained indicate that the data given are quite accurate. Considerably greater variations may be observed in the case of doubly charged anions. The heats of formation of gaseous CO_3^{2-} and SO_4^{2-} are -35 ± 9 and -157 ± 12 kcal, respectively. Similarly to oxides and sulfides, the calculated lattice energy values for Na_2CO_3 and Na_2SO_4 differ most from the experimental values.

The extremely large variations in the calculated values for heats of formation of the ion CrO_4^{2-} indicate, apparently, considerable counter polarization in the crystal lattices of $CaCrO_4$ and $BaCrO_4$. The ion CrO_4^{2-} has a tendency to deform, which is shown by the deviation of its form from a regular tetrahedron. This case shows that it is possible to calculate the lattice energies from the radii for salts formed from rigid, slightly deformed ions.

The lattice energies for NH_4Cl, NH_4Br and NH_4I (equal to 163.3, 157.2 and 148.2 kcal) were calculated by equation (1). The heat of formation of gaseous NH_4^+, which is equal to $\Delta H_{298} = 147.9 \pm 0.7$, was calculated from the above and from thermochemical data [9]. The lattice energies of ammonium salts were then calculated by equation (1) and from thermochemical data using the equation:

$$U = \Delta H_C + \Delta H_A - \Delta H_{CA}, \qquad (2)$$

where ΔH_C and ΔH_K are the heats of formation of gaseous cation and anion, respectively, while ΔH_{CA} is the heat of formation of the crystalline salt (Table 4).

The values of the lattice energies of NH_4NO_3, NH_4CNS, NH_4HSO_4, NH_4CN, NH_4HS, were calculated by two separate methods which were very similar. The experimental values of the lattice energies are higher in the cases of NH_4F, NH_4NO_2, NH_4HCO_3, NH_4CNO, NH_4CH_3COO than those calculated by Equation (1). It is known that the hydrogen bond N-H...F, is formed in NH_4F crystals and the difference in lattice energy values (6 kcal) is close to the energy of the hydrogen bond. It is possible that the hydrogen bond of the type: N—H...ONO, N—H...OCN, etc. also forms in the other cases mentioned above. It is also noteworthy that the experimental value of the lattice

energy of NH_4ClO_4 is less than that calculated by Equation (1). Possibly, it is this factor which explains the relatively high solubility of ammonium perchlorate in comparison with perchlorates of potassium, rubidium and cesium.

TABLE 4

Lattice Energies of Ammonium Salts

Salt formula	Lattice energy		Difference	Salt formula	Lattice energy		Difference
	by equation (1)	from thermochemical data			by equation (1)	from thermochemical data	
NH_4F	188.7	195	6.1	NH_4CN	162.9	165	2
NH_4NO_2	175.5	182	6	NH_4HS	157.6	161	8
NH_4HCO_2	174.1	179	5	NH_4NO_3	160.1	157	−3
$NH_4CH_3CO_2$	172.5	178	5	NH_4CNS	157.6	158	0
NH_4CNO	172.5	180	7	NH_4HSO_4	153.3	153	0
				NH_4ClO_4	142.8	138	−5

Equation (2) may be used for the evaluation of the heats of formation of a series of salts. Lattice energy values, calculated by Equation (1) (Tables 1-3) and heats of formation of the corresponding gaseous ions could be used for this purpose. The heats of formation of some salts, evaluated by this method using Equation (2) are given in Table 5.

It is especially interesting to evaluate the heats of formation of unknown compounds by this method to try to obtain data on their stability.

The heats of formation of alkali-earth metal bicarbonates and hydrosulfides calculated by Equation (2) are given in Table 6.

TABLE 5

Heats of Formation of Some Compounds

Rubidium and cesium salts	Heat of formation	Alkali-earth metal salts	Heat of formation
Rb_2Se	− 68 ± 4	$Ca(CNO)_2$	−203 ± 2
Cs_2Se	− 66 ± 4	$Sr(CNO)_2$	−203 ± 2
RbCN	− 25 ± 2	$Ca(CNS)_2$	− 80 ± 4
CsCN	− 27 ± 2	$Sr(CNS)_2$	− 87 ± 2
RbCNO	− 95 ± 1	$Ba(CNS)_2$	− 99 ± 4
CsCNO	− 96 ± 1	$Ca(ClO_3)_2$	−166 ± 2
CsCNS	− 50 ± 2	$Ca(ClO_4)_2$	−164 ± 2
$RbNO_2$	− 86 ± 1	$Sr(ClO_4)_2$	−177 ± 2
$CsNO_2$	− 85 ± 1	$Ca(MnO_4)_2$	−343 ± 2
$RbHCO_2$	−155 ± 1	$Sr(MnO_4)_2$	−357 ± 2
$CsHCO_2$	−156 ± 1	$Ba(MnO_4)_2$	−373 ± 2
$RbCH_3CO_2$	−171 ± 1		
$CsCH_3CO_2$	−171 ± 1		

On the basis of these values the heats of reactions of the type:

(I)

(II)

Could be evaluated.

TABLE 6

Compound	ΔH°_{298}	Changes in thermodynamic functions in reactions (I) and (II)		
		ΔH	$T\Delta S$	ΔZ
$Ca(HCO_3)_2$	−463 ± 7	12 ± 7	15 ± 1	− 3 ± 7
$Sr(HCO_3)_2$	−464 ± 6	10 ± 6	15 ± 1	− 5 ± 6
$Ba(HCO_3)_2$	−472 ± 6	18 ± 6	15 ± 1	+ 3 ± 6
$Ca(HS)_2$	−107 ± 5	−13 ± 5	7 ± 2	−20 ± 7
$Sr(HS)_2$	−114 ± 5	1 ± 5	7 ± 2	− 6 ± 7
$Ba(HS)_2$	−126 ± 5	16 ± 5	7 ± 2	9 ± 7

The heats of decomposition of bicarbonate and hydrosulfide are given in Table 6. The entropy change in reaction (I) is evaluated using the entropy change in $NaCO_3$ decomposition. This value should remain constant for all the reactions of type (I) according to the rule of constant entropy change for the same type of reaction [10].

Kobozev's rule [11] was applied for the evaluation of the entropy change in reaction (II).

The change ΔZ, found from the values of ΔH and ΔS is negative in all cases except for $Ba(HCO_3)_2$ and $Ba(HS)_2$. Consequently, the bicarbonates and hydrosulfides of calcium and strontium are unstable in the thermodynamic sense.

SUMMARY

1. The values of lattice energies were calculated for hydroxides, hydrosulfides, hydroselenides, cyanides, cyanates, thiocyanates, nitrites, formates, acetates, bicarbonates, nitrates, chlorates, perchlorates, permanganates, carbonates and sulfates of alkali and alkali-earth metals. The heats of formation of the corresponding gaseous anions were calculated.

2. The heats of formation of a series of ammonium salts and of the gaseous ammonium ion were calculated.

3. The heats of formation of some rubidium, cesium, calcium, strontium and barium salts were evaluated.

LITERATURE CITED

[1] A. F. Kapustinsky and K. B. Yatsimirsky, J. Gen. Chem. 26, 941 (1956). (T. p. 1069).*

[2] A. F. Kapustinsky, J. Gen. Chem. 13, 497 (1943).

[3] K. B. Yatsimirsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1947, 453.

[4] A. F. Kapustinsky and K. B. Yatsimirsky, J. Gen. Chem. 19, 2191 (1949) (T. p. a-665).*

[5] K. B. Yatsimirsky, The Thermochemistry of Complex Compounds (Acad. Sci. USSR Press, Moscow, 1951).

[6] J. Sakamoto, Bull. Chem. Soc. Japan 26, 283 (1953).

[7] R. Juza, Z. anorg. u. allgem. Chem. 231, 121 (1937).

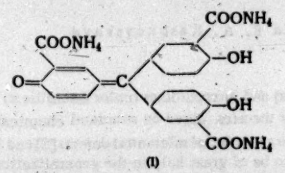
[8] C. D. West, J. Phys. Chem. 39, 493 (1935).

[9] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and J. Jaffe, Selected Values of Chem. Therm. Properties (Washington, 1952), Circ. 500.

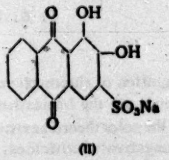
*T. p. = C. B. Translation pagination.

It would be possible to evaluate numerically the auxochrome effect of each element if exact values of such relations were obtained for compounds of many elements with the same type of reagents. These relative numerical characteristics of the elements would, as has already been mentioned above, remain constant for all analogous colored compounds formed by these elements and reagents of the same type. Thus, if C and D – radicals of monotypic reagents – have identical reactions with the elements A and B, then $\epsilon_{mol\ AC}/\epsilon_{mol\ BC} = \epsilon_{mol\ AD}/\epsilon_{mol\ BD}$, etc.

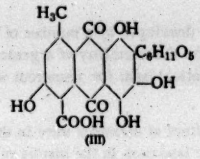
The above considerations were checked by studying the optical properties of the analytical reaction products of aluminon (I), alizarin S (II), carminic acid (III) and hydroxyaurintricarboxylic acid (IV) with the following cations: VO_2^{2+}; UO_2^{2+}; Fe^{3+}; Cu^{2+}. *



(I)



(II)



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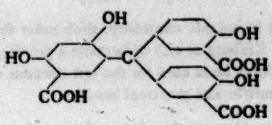

(IV)

EXPERIMENTAL

First we found the optimal conditions (i. e. time, temperature and the pH of the medium) for carrying out the reaction and plotting the corresponding absorption curves on a Pulfrich photometer. For calculation of ϵ_{mol} the composition of the complex was determined by the method of Ostromyslensky – Job – Babko [8-10].

The experimental results and calculated data are given below.

First of all, as an example, in Table 1 we give the data from the investigation of the composition of aluminon complexes with some cations by the usual method.

TABLE 1

Data on the Composition of Aluminon Complexes

Cation (ct)	Solutions measured	Optical density with molar ratio reagent : cation							
		1:5	1:4	1:3	1:2	1:1	2:1	3:1	4:1	5:1
Fe^{3+}	ct + reagent	0.30	0.33	0.40	0.55	0.72	0.73	0.66	0.61	0.58
	reagent	0.05	0.06	0.07	0.09	0.10	0.13	0.14	0.16	0.18
	difference	0.25	0.27	0.33	0.46	0.62	0.60	0.52	0.45	0.40
UO_2^{2+}	ct + reagent	0.18	0.22	0.26	0.31	0.41	0.40	0.28	0.27	0.26
	reagent	0.03	0.05	0.06	0.08	0.10	0.12	0.16	0.17	0.18
	difference	0.15	0.17	0.20	0.23	0.31	0.28	0.12	0.10	0.08
VO^{2+}	ct + reagent	0.27	0.31	0.39	0.48	0.62	0.59	0.50	0.45	0.38
	reagent	0.04	0.05	0.07	0.09	0.10	0.12	0.15	0.16	0.17
	difference	0.23	0.26	0.32	0.39	0.52	0.47	0.35	0.29	0.21

* In carrying out this part of the investigation we developed photocolorimetric methods of determining uranyl and vanadyl in pure solutions, which could be employed for this purpose.

From the data given in Table 1, it is very clear that in the complex-formation reactions examined, one molecule of aluminon reacts with one cation of the elements in question. Identical data were also obtained by us for the other complex formation reactions studied.

More data is summarized in Table 2, characterizing the final reaction products of cations with the reagents; in this and the following tables the Roman figures denote the reagents, whose structural formulas were given earlier with the same figures.

ERRATA TO THIS ISSUE

[J. Gen. Chem. 26, No. 9 (1956)]

1) The following equations should be inserted at the bottom of p. 2658 of this issue:

$$M(HCO_3)_2 = MCO_3 + H_2O + CO_2, \quad (I)$$
$$M(HS)_2 = MS + H_2S. \quad (II)$$

2) The following equation should be inserted below Table 3, p. 2670 of this issue:

$$D\left(\frac{105}{T}\right) + 3E\left(\frac{185}{T}\right) + E\left(\frac{454}{T}\right) + 2E\left(\frac{808}{T}\right) = Co$$

Products of the Cations and

Reagent		
	III	IV
3	5.57	4.05
)	530	530
10^3	$1.31 \cdot 10^4$	$1.30 \cdot 10^3$
7	5.57	3.79
)	570	500
10^3	$8.83 \cdot 10^3$	$8.48 \cdot 10^3$
7	—	—
)	—	—
10^3	—	—
7	—	—
)	—	—
10^4	—	—

the molar extinction coefficient of the
nother cation with the same reagent in a
e mol of the reaction products of these

omplex Compounds of Some

formed by the cations		
$^{2+}$ / $^{3+}$	Fe^{2+} / UO_2^{+}	Cu^{2+} / UO_2^{+}
18	1.86	1.49
30	2.00	1.54
—	—	—
—	—	—

From the data given in Table 1, it is very clear that in the complex-formation reactions examined, one molecule of aluminon reacts with one cation of the elements in question. Identical data were also obtained by us for the other complex formation reactions studied.

More data is summarized in Table 2, characterizing the final reaction products of cations with the reagents; in this and the following tables the Roman figures denote the reagents, whose structural formulas were given earlier with the same figures.

TABLE 2

Some Characteristics of the Reactions and the Reaction Products of the Cations and Reagents Examined

Cation	Characteristic of the reaction product	Reagent I	Reagent II	Reagent III	Reagent IV
VO^{2+}	Optimal pH	3.72	5.23	5.57	4.05
	λ max	530	500	530	530
	ϵ mol	$3.76 \cdot 10^3$	$9.40 \cdot 10^3$	$1.31 \cdot 10^4$	$1.30 \cdot 10^3$
UO_2^{2+}	Optimal pH	3.49	5.57	5.57	3.79
	λ max	530	570	570	500
	ϵ mol	$2.48 \cdot 10^3$	$6.10 \cdot 10^3$	$8.83 \cdot 10^3$	$8.48 \cdot 10^3$
Cu^{2+}	Optimal pH	4.05	5.57	—	—
	λ max	530	500	—	—
	ϵ mol	$3.70 \cdot 10^3$	$9.40 \cdot 10^3$	—	—
Fe^{3+}	Optimal pH	3.79	5.37	—	—
	λ max	530	530	—	—
	ϵ mol	$4.36 \cdot 10^3$	$1.22 \cdot 10^4$	—	—

From the data given in Table 2, it is obvious that the ratio of the molar extinction coefficient of the reaction product of a cation with the reagent examined, to that of another cation with the same reagent in a series of cases completely coincides with the value of the ratio of ϵ_{mol} of the reaction products of these cations with other reagents.

For clarity, these data are given in Table 3.

TABLE 3

The Ratio of the Molar Extinction Coefficients of the Complex Compounds of Some Cations

Reagent	Ratio of ϵ_{mol} of the complexes formed by the cations: $\frac{VO^{2+}}{UO_2^{2+}}$	$\frac{VO^{2+}}{Cu^{2+}}$	$\frac{Fe^{3+}}{VO^{2+}}$	$\frac{Fe^{3+}}{Cu^{2+}}$	$\frac{Fe^{3+}}{UO_2^{2+}}$	$\frac{Cu^{2+}}{UO_2^{2+}}$
I	1.50	1.00	1.16	1.18	1.86	1.49
II	1.54	1.00	1.30	1.30	2.00	1.54
III	1.49	—	—	—	—	—
IV	1.51	—	—	—	—	—

From these data it follows that if we take the auxochrome effect of uranyl as 100, then the analogous characteristic of the other cations will be: Fe^{3+} = 190, VO^{2+} = 150, Cu^{2+} = 150.

Thus it is possible to arrange the cations examined in the following series according to their auxochrome effect in compounds where they are directly linked to oxygen atoms:

$$Fe^{3+} > VO^{2+} > Cu^{2+} > UO_2^{2+}.$$

This series may be supplemented by other cations after the investigation of their colored compounds with some organic reagents, in the molecules of which the object of ionic attack is an oxygen atom, as in the materials we investigated.

SUMMARY

Rules by which the relative color effect of elements or cations may be evaluated are quite unnecessary as they only confirm the fact that the concepts of the auxochrome-chromophore character of elements, developed in organic-reagent chemistry, reflect real phenomena which can be characterized numerically. Furthermore, after a more thorough investigation, the facts examined will make it possible to predict, more or less accurately, the order of magnitude of the molar extinction coefficient of corresponding complex compounds, the sensitivity of some colorimetric analytical reactions, and to ascertain the composition of the complexes.

LITERATURE CITED

[1] R. Vitsinger, Organic Dyes (Chem. Theoret. Press, Leningrad 1936).

[2] A. N. Terenin, Photochemistry of Dyes (Acad. Sci. USSR Press, 1947), 41.

[3] V. I. Kuznetsov, Thesis: Procedures for Finding Color Reactions for Inorganic Ions (Moscow, 1948).

[4] V. I. Kuznetsov, Progr. Chem. 21, 175 (1952).

[5] L. M. Kulberg, Organic Reagents in Analytical Chemistry (State Chem. Press, 1950).

[6] L. M. Kulberg, A. A. Ponomarev and N. I. Davydova, J. Anal. Chem. 9, 85 (1954) (T. p. 97).*

[7] A. T. Terentyev and E. G. Rukhadze, Sci. Repts. Moscow State Univ. 132, 197 (1950).

[8] I. Ostromyslensky, Ber. 44, 268 (1911).

[9] P. Job, Ann. 9, 113 (1928).

[10] A. K. Babko, J. Gen. Chem. 18, 816 (1948).

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*T. p. = C. B. Translation pagination.

THE DETERMINATION OF THE TRUE SPECIFIC HEAT OF SOLID MATERIALS AT LOW TEMPERATURES

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One of the main problems in calorimetry is the experimental determination of the specific heat of various materials over the widest possible range of temperatures. The equipment in the Liginin Thermal Laboratory measures the specific heat at average and high temperatures with great accuracy.

The aim of our work was to construct instruments and calorimetric equipment for determining specific heats at low temperatures and also to investigate the specific heats of certain solid materials.

This problem is not a new one: in 1938 N. N. Feodosyev[1] carried out a comparative investigation of the applicability of adiabatic and isothermal methods for measuring specific heats and measured the specific heat of potassium chloride over the range from 86 to 290°K. However, there was no apparatus ready for our use, so we had to make a new calorimeter for determining specific heats at low temperatures. An efficient vacuum calorimeter with an adiabatic shielding case was used in the present work also; the thermal laboratory apparatus constructed by N. N. Feodosiev [1] was used as a basic prototype for the calorimetric apparatus. The changes made were mainly concerned with temperature measurement, the layout of the calorimetric vessel and the maintenance of adiabatic conditions.

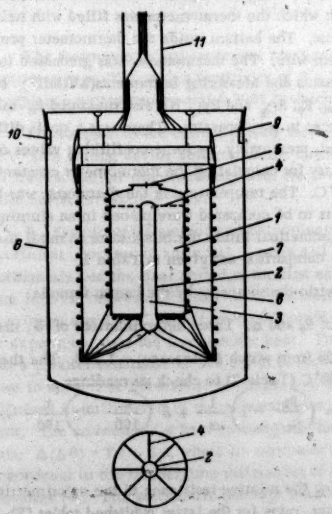

Fig. 1. The position of parts of the calorimeter in the vacuum chamber. Explanation in text.

*Deceased.

1. Calorimetric apparatus (Fig. 1). The calorimeter (1) is, strictly speaking, a copper cylinder with a volume of approximately 35 ml, gold plated on the exterior to decrease radiation emission and suspended by three silk threads from the cover of the adiabatic case. A copper tube (2) was soldered into the bottom of the calorimeter and served as the compartment for the thermometer (3), which measured the calorimeter's temperature and the raise in the temperature in the experiment. Eight radial baffles (4) of copper foil 0.1 mm thick were soldered with tin to the inner surface of the calorimeter and to the central tube, and were used for rapid temperature adjustment inside the calorimeter. For the same reason, after the material had been placed in the calorimeter, it was filled with dry hydrogen through the opening in the top (5). A second thermometer (6) consisting of a platinum wire of "extra" grade of 0.05 mm diameter and having a resistance of approximately 100 Ω was placed on the outer surface of the calorimeter. The thermometer (6) covered almost all the surface of the side uniformly and was used to maintain equal temperatures in the calorimeter and its case. A constantan wire of 0.03 mm diameter and 650 Ω resistance laid in the bottom of the calorimeter acted

as heater. The adiabatic case (7) was made from sheet copper 1 mm thick and a constantan heater with 1000 Ω resistance and a platinum thermometer with 100 Ω resistance at 0°C were placed on the outer surface of the cylindrical part. A bakelite lacquer with excellent insulating properties, was used for fastening on the thermometer and heaters. The case and calorimeter thermometers formed adjacent arms of a bridge (bolometer system); the two other arms were formed by standard resistances of 100 Ω each, to one of which a hexadecade resistance box for 100,000 Ω was connected in parallel. Differences of 0.0001° between the calorimeter and case temperatures could be recorded by using such a bridge, and this system was considerably more sensitive than the thermocouples usually used for this purpose. The current in the case heater was regulated manually, the difference in calorimeter and case temperatures was not greater than 0.001°.

The vacuum chamber was a copper beaker (8), and the ring (9), adiabatic case (7) and calorimeter (1) were suspended from its top. A projection was silver-soldered into the upper part of the chamber which ensured that the top was always placed in one definite position during the assembly of the chamber. A massive copper collar, first heated with a blow torch, was placed on the upper part of the installed vacuum chamber to seal it. A thin argentan pipe (11) was silver-soldered into the top of the vacuum chamber and was used for pumping out the chamber and to lead in the supply mains.

The system was evacuated with an oil diffusion pump MM-40A and the pressure was measured with a combined vacuum gage VK-1. Heat exchange by convection and the heat conductivity of the gas was practically completely excluded with a vacuum of $2\text{-}4 \cdot 10^{-6}$ mm Hg, which was usually attained in the chamber. The effect of radiation emission is negligible at low temperatures. The supply mains were attached to the ring (9) and the adiabatic case (7) and were thus heated to a temperature equal to that of the calorimeter so as not to transfer a considerable amount of heat.

Liquid nitrogen, a mixture of solid carbon dioxide and alcohol and ice were used as cooling agents. Temperatures lower than 78°K were obtained by pumping out nitrogen vapor. The lowest temperature achieved in the experiments was 58°K.

2. Measurement of temperature and energy. A platinum resistance thermometer was especially made for measuring the calorimeter temperature. A platinum wire of "extra" grade was wound onto a mica cross with very low tension to ensure the stability of thermometer readings. The sensitive element of the thermometer was placed in a platinum case sealed to a small glass nozzle through which the thermometer was filled with helium. Four leads of the same type of platinum were sealed into the glass. The helium inside the thermometer provided a good heat conductor between the walls of the case and platinum wire. The thermometer was graduated in the Cryogenic Laboratory of the Moscow State Institute of Measurements and Measuring Instruments (MGIMIP) by A. S. Borovik-Romanov and D. I. Sharevskaya who measured R_{100}, R_0, R_{O_2} and R_{H_2}. We also measured R_0 using the instruments intended for measuring the thermometer resistances in our apparatus. There was a small difference between our data and those of MGIMIP which could be explained, presumably, by some conflicting values of the standard resistances. We obtained the missing fifth point necessary for calculating the thermometer constants by comparing with a standard thermometer in a thermostat at + 50°C. The temperature in the thermostat was kept constant with an accuracy of ± 0.005°. Both of the thermometers to be compared were placed in an aluminum block which was immersed in the thermostat; the temperature fluctuations inside the block were so small that they were not recorded by the thermometers. The results of one comparison are given in Table 1.

The constant δ may easily be calculated for the calorimetric thermometer by the known formula: $t°C = \left(\frac{R}{R_0} - 1\right)\frac{1}{\alpha} + \delta\left(\frac{t}{100} - 1\right)\cdot\frac{t}{100}$, using the values of R_0 and α. Three determinations of δ, made at different times, gave the following results: 1.485, 1.489, 1.489 from which δ (average) = 1.488. The thermometer was compared with a standard one in the same thermostat at + 25°C (Table 2) to check its readings.

The constant β is easily calculated by the equation $t°C = \left(\frac{R_t}{R_0} - 1\right)\frac{1}{\alpha} + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} + \beta\frac{t^3}{100^3}\left(\frac{t}{100} - 1\right)$, using the data for the oxygen point.

Temperatures below − 190°C were calculated by converting the relative resistance of the calorimetric thermometer to the relative resistance of the standard thermometer, using for the latter published tables [2], according to R. G. Strelkov's formula [3]:

$$W_T = W_{H_2} + \frac{W_{O_2} - W_{H_2}}{W'_{O_2} - W'_{H_2}} (W'_T - W'_{H_2}),$$

where W' is the relative resistance and W is the standard relative resistance.

TABLE 1

Comparison of a Standard and Calorimetric Thermometer at + 50°C.

Time (in min.)	Thermometer resistance (in ohms)	
	standard	calorimetric
1	12.4744_7	
5		70.7910_2
6	12.4744_8	
8		70.7908_7
10	12.4744_7	
14		70.7910_9
16	12.4745_3	
20		70.7911_0
22	12.4744_5	
Average	12.4744_8	70.7910_2
Temperature	49.354_5°C	

TABLE 2

Comparison of a Standard and Calorimetric Thermometer at + 25°C.

Time (in min.)	Thermometer resistance (in ohms)	
	standard	calorimetric
2	11.5047_1	
3		65.3193_8
4	11.5046_8	
6		65.3195_5
7	11.5047_5	
9		65.3196_5
10	11.5047_4	
12		65.3194_8
13	11.5047_8	
15		65.3192_1
16	11.5047_7	
18		65.3191_2
19	11.5047_7	
21		65.3195_8
Average	11.5047_4	65.3194_2
Temperature	25.738_4°C	25.737_7°C

The thermometer resistance was measured by a Disselhorst five decade potentiometer, and a Tsernik galvanometer, type "C", with a sensitivity of $S = 3.5 \cdot 10^{-8} - 2 \cdot 10^{-7}$ V, acted as a zero instrument. The accuracy of resistance measurements was 0.0001 Ω which gave temperature readings of an accuracy of up to 0.0004°.

The strength of the current passing through the calorimeter heater was measured with a potentiometer PPTV-1. A timing device determined the duration of the current flow and with a mechanical fitting the former switched on and off simultaneously with the switching over of the accumulator battery from the ballast circuit to the heater circuit and back.

3. Experimental method and determination of the thermal value of the calorimeter. The calorimetric experiment consisted of an initial, a main and a final period. Two calorimetric experiments were conducted continuously and the final period of the first experiment acted as the initial period of the second. The temperature interval between such pairs of experiments was, on the average, 10°. The temperature rise in a separate experiment was 1-1.5° so that we could consider that the specific heat, referred to the average temperature of the experiment, was the true specific heat. The bridge bolometric system was balanced before the experiment with a parallel resistance of 100,000 Ω in such a way that the initial temperature drift of the calorimeter was close to zero. The bolometric readings, i. e. the amount the bolometric system was off balance, which was registered in millimeters of the galvanometer scale, were kept under observation during the whole of the experiment. The correction for heat exchange of the calorimetric system with the outer surroundings consists of two parts: $\Delta(\Delta\vartheta) = \Sigma v + \Sigma w$, where Σv combines all the factors which induce transmission of a quantity of heat, proportional to the temperature differences of the calorimeter and the case, and Σw is a heat exchange, constant with time [4]. The bolometric readings were used for calculating the first part of the heat exchange correction. The second part of this correction was calculated from the temperature drift in the calorimeter during the initial

and final periods. The initial and final drifts were small and were usually not greater than $5 \cdot 10^{-5}$ Ω per minute. The correction for heat exchange, as a rule, was not greater than 0.5% of the temperature rise. This correction became somewhat greater at temperatures close to room temperatures, due to the considerable increase in radiation emission and at 298°K it was approximately 1% of the total temperature rise.

The thermal value of the calorimeter was determined from a number of experiments with potassium chloride whose specific heat at low temperatures had been thoroughly studied by P. G. Strelkova [3, 5], N. N. Feodoseva [1], K. Kluziusa [6], et al. Chemically pure potassium chloride was heated at 650-700°C for 24 hours. After cooling over phosphoric anhydride, the slightly sintered powder was ground in an agate mortar and then dried again in a vacuum at 220°C to constant weight. A series of experiments were carried out with the calorimeter filled with the dry salt, at a temperature range from 60 to 300°K. The thermal value of the empty calorimeter was the difference between the thermal value of the system, determined experimentally and the specific heat of the given quantity of salt. The thermal value of the empty calorimeter relative to temperature, obtained in experiments with potassium chloride, is given in Fig. 2.

4. The specific heat of benzoic acid. The measurement of the specific heat of benzoic acid was undertaken for checking the methods used, as this product can be obtained readily in a very pure state and could be used as a standard material for checking and comparing various types of calorimeters in specific heat determinations in the range from 10 to 350°K [7]. The specific heat of benzoic acid was determined in the range 10-410°K with an accuracy of 0.2% by Furukawa, McCoskey and King [8], who used a sample containing not more than 0.003 mol.% of impurity. The specific heat of the acid is given in Park's work [9] from 93 to 295°K with an accuracy of 1%; Park's data is in agreement with the previous work within the limits of accuracy of the experiment. The specific heat of benzoic acid at low temperatures had been determined only in these two papers; however, several investigations had been carried out at close to room temperatures and their results differ from the above by 5 to 25% [8].

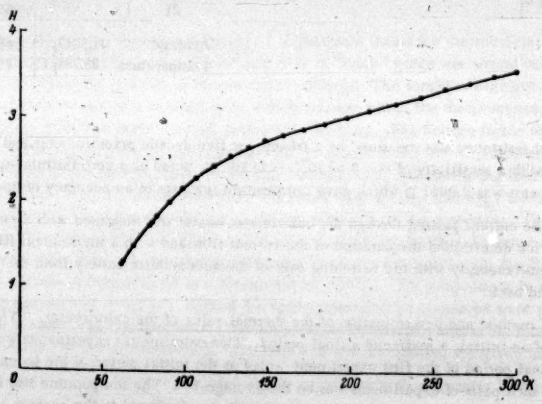

Fig. 2. Thermal value of the empty calorimeter.

The benzoic acid sample used for determining specific heat was prepared in the All-Union Scientific Research Institute of Metrology and Standardization. The results of measuring the specific heat of benzoic acid are given in Table 3 and Fig. 3. The deviation of experimental points from the smooth specific heat curve does not exceed 0.3% except for very rare exceptions. The data of Furukawa, McCoskey and King [8] differ from the results obtained by us by not more than 0.5% in the range 210-270°K and by not more than 0.3% at all other temperatures.

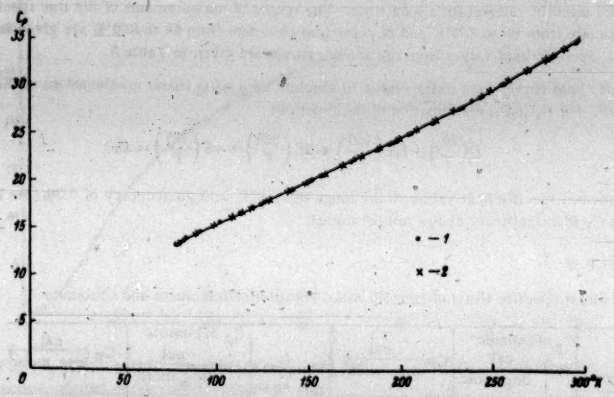

Fig. 3. Molar specific heat of benzoic acid. 1) Our experiments; 2) data of Furukawa, McCoskey and King [8].

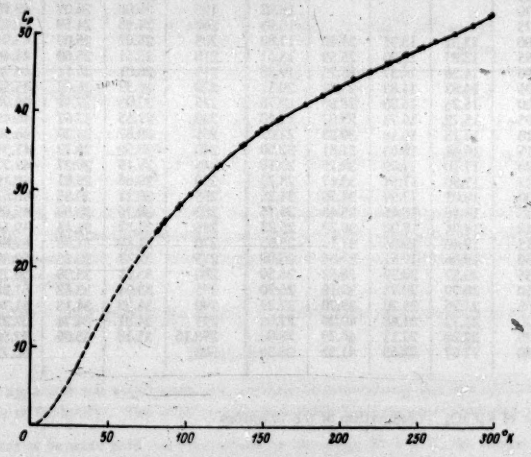

Fig. 4. Molar specific heat of potassium dichromate. Full curve – experimental points, dotted curve – extrapolation to 0°K.

5. Determination of the specific heat of potassium chromate and dichromate, and calculation of thermodynamic parameters. The calorimeter described was used for determining the specific heat of potassium chromate and dichromate. The above salts undergo polymorphous conversions at high temperatures: K_2CrO_4 at 664°C and $K_2Cr_2O_7$ at approximately 250°C. The true specific heat of potassium dichromate was investigated in the range from 111 to 385°C by G. L. Galchenko [10]. The specific heats of these salts have not been deter-

mined at low temperatures. V. A. Kireev calculated the standard thermodynamic parameters for K_2CrO_4 by comparative calculation [11]; the thermodynamic parameters of $K_2Cr_2O_7$ were not known. The given salts were recrystallized and dried in vacuum for a long time. The results of measurements of the true specific heats of potassium dichromate from 80 to 300°K and of potassium chromate from 60 to 300°K are given in Table 3 and in Figs. 4 and 5. Specific heat values from the smooth curves are given in Table 3.

The specific heat curves were extrapolated to absolute zero using linear combinations of the Debye-Einstein functions. For $K_2Cr_2O_7$, combination of the functions

$$D\left(\frac{70}{T}\right) + 3E\left(\frac{150}{T}\right) + 3E\left(\frac{330}{T}\right) + 4E\left(\frac{795}{T}\right) = Cv$$

gave the experimental specific heat values in the range 80-150°K with an accuracy of 0.3% (the difference between C_p and C_v is insignificant at low temperatures).

TABLE 3

True Molar Specific Heats of Benzoic Acid, Potassium Dichromate and Chromate

Temperature °K	C_p of benzoic acid $\left(\frac{cal}{deg.\ mole}\right)$		$C_p\left(\frac{cal}{deg.\ mole}\right)$		Temperature °K	C_p of benzoic acid $\left(\frac{cal}{deg.\ mole}\right)$		$C_p\left(\frac{cal}{deg.\ mole}\right)$	
	our data	data from [8]	$K_2Cr_2O_7$	K_2CrO_4		our data	data from [8]	$K_2Cr_2O_7$	K_2CrO_4
60				13.93	185	23.14	23.12	41.85	28.72
65				15.01	190	23.61	23.60	42.37	29.06
70				16.02	195	24.08	24.09	42.90	29.40
75				16.93	200	24.55	24.59	43.42	29.72
80	13.32	13.35	24.40	17.80	205	25.03	25.09	43.94	30.04
85	13.87	13.90	25.59	18.61	210	25.51	25.60	44.46	30.35
90	14.36	14.37	26.73	19.38	215	26.01	26.11	44.98	30.65
95	14.82	14.83	27.82	20.11	220	26.52	26.62	45.48	30.94
100	15.28	15.28	28.86	20.76	225	27.03	27.14	45.96	31.22
105	15.72	15.73	29.87	21.40	230	27.55	27.67	46.45	31.50
110	16.18	16.18	30.85	22.02	235	28.07	28.20	46.90	31.77
115	16.64	16.63	31.81	22.60	240	28.59	28.73	47.34	32.03
120	17.10	17.09	32.75	23.18	245	29.19	29.27	47.77	32.29
125	17.56	17.54	33.67	23.73	250	29.66	29.81	48.19	32.54
130	18.02	17.99	34.56	24.26	255	30.21	30.35	48.61	32.79
135	18.48	18.45	35.43	24.75	260	30.76	30.89	49.02	33.03
140	18.94	18.90	36.29	25.23	265	31.32	31.43	49.44	33.27
145	19.40	19.36	37.10	25.63	270	31.89	31.98	49.88	33.51
150	19.86	19.81	37.85	26.09	275	32.47	32.53	50.33	33.75
155	20.32	20.27	38.52	26.50	280	33.05	33.08	50.79	33.99
160	20.79	20.73	39.12	26.90	285	33.64	33.63	51.26	34.23
165	21.26	21.20	39.70	27.29	290	34.23	34.18	51.74	34.48
170	21.73	21.68	40.26	27.66	295	34.81	34.74	52.23	34.73
175	22.20	22.15	40.79	28.03	298.16	35.18	35.09	52.50	34.90
180	22.67	22.63	41.32	28.38	300			52.73	34.99

In the case of K_2CrO_4, combination of the functions

gave experimental specific heat values from 60 to 300°K with an accuracy of 1% and in the range 60-160°K with an accuracy of 0.3%.

The enthalpy and entropy were calculated in the given temperature range by numerical integration with the values, taken from the graphs of C_p - T and C_p - log T, at equal intervals. The calculation was carried out by the chosen combinations of the Debye-Einstein functions from 0°K to the lowest measurement limit. The

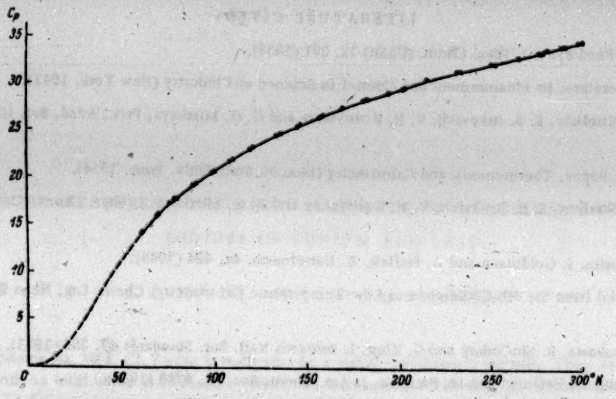

Fig. 5. Molar specific heat of potassium chromate. Full curve – experimental points, dotted curve – extrapolation to 0°K.

TABLE 4

Enthalpy, Entropy and Isobaric-Isothermal Formation Potentials from Elements for K_2CrO_4 and $K_2Cr_2O_7$ at 298.16°K

Material	$H\left(\frac{cal}{mole}\right)$	$S\left(\text{energy units}\right)$	ΔS^0 (energy units)	$\Delta Z^0\left(\frac{cal}{mole}\right)$
K_2CrO_4 (Kireev's comparative method)	–	46.2 ± 2.0	– 87.4	– 307350
K_2CrO_4 (Our data)	6806 ± 30	47.8 ± 0.8	– 86.3 ± 1.3	– 307700
$K_2Cr_2O_7$	9850 ± 80	69.6 ± 1.7	– 143.8 ± 2.3	– 445600

standard entropies of formation of K_2CrO_4 and $K_2Cr_2O_7$ were calculated from the standard entropies of the elements, taken from tables [12]. The isobaric-isothermal formation potentials were calculated by heats of formation, taken from tables and converted to 298.16°K. The calculated thermodynamic parameters for potassium chromate and dichromate are given in Table 4.

The results obtained by V. A. Kireev by the method of comparative calculation are given for comparison.

SUMMARY

1. A calorimetric apparatus was constructed and checked for determining the true specific heats of solid materials at temperatures of 60-300°K. The relative error in specific heat measurements was ± 0.3%.

2. The specific heat of benzoic acid was determined for the range 80-300°K; the results of the measurement agreed with the literature data within the limits of experimental accuracy.

3. The true specific heats of potassium chromate and dichromate were measured in the ranges 60-300°K and 80-300°K respectively. It was found that these materials did not undergo polymorphous conversion in the given ranges. The enthalpies, entropies and isobaric-isothermal formation potentials at 298.16°K were calculated for K_2CrO_4 and $K_2Cr_2O_7$. The thermodynamic parameters, calculated for K_2CrO_4 by V. A. Kireev's comparative method, agree reasonably with those calculated from experimental data.

LITERATURE CITED

[1] N. N. Feodosyev, J. Phys. Chem. (USSR) 12, 291 (1938).

[2] Temperature, its Measurement and Control in Science and Industry (New York, 1941).

[3] P. G. Strelkov, E. S. Itskevich, V. N. Kostryukov and G. G. Mirskaya, Proc. Acad. Sci. USSR 85, 1085 (1952).

[4] M. M. Popov, Thermometry and Calorimetry (Moscow State Univ. Press, 1954).

[5] P. G. Strelkov, E. S. Itskevich, V. N. Kostryukov and G. G. Mirskaya, J. Phys. Chem. (USSR) 28, 645 (1954).

[6] K. Clusius, J. Goldmann and A. Perlick, Z. Naturforsch. 4a, 424 (1949).

[7] Material from the 4th Conference on Low-Temperature Calorimetry, Chem. Eng. News 27, 2772 (1949).

[8] G. Furukawa, R. McCoskey and G. King, J. Research Natl. Bur. Standards 47, 256 (1951).

[9] G. Parks, H. Huffman and M. Barmore, J. Am. Chem. Soc. 55, 2733 (1933).

[10] M. M. Popov and G. L. Galchenko, J. Gen. Chem. 21, 2220 (1951) (T. p. 2489).*

[11] V. A. Kireev, J. Gen. Chem. 17, 1229 (1947).

[12] E. V. Britske, A. F. Kapustinsky, B. K. Veselovsky, L. M. Shamovsky, L. G. Chentsova and B. I. Anvaer, Thermal Constants of Inorganic Materials (Acad. Sci. USSR Press, 1949).

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THE IRREVERSIBLE RECIPROCAL SYSTEM OF CHLORIDES AND IODIDES OF SODIUM AND LEAD

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The systems Na, Pb ‖ Cl, I were investigated by a visual-polythermal method. They were melted in hard glass tubes with an inlet tube. A Nichrome-constantan thermocouple was used. A continuous stream of dry CO_2 was passed through the tube to avoid iodide oxidation. All the data in the tables and figures are expressed in equivalent percentages.

The comparative heat effect of the exchange reaction in the system Na, Pb ‖ Cl, I is equal to 7.75 kcal per equiv. in the direction of the stable diagonal section PbI_2 and Na_2Cl_2:

$$PbCl_2 + 2NaI \rightarrow PbI_2 + 2NaCl,$$

$$85.5 + 138.56 \quad 42.9 + 196.66.$$

Double systems. 1) Na_2Cl_2–Na_2I_2 were investigated by M. Amadori [1] and Schobert [2]. The eutectic point lies at 578° and 36% Na_2Cl_2. There are limited solid solutions in the range from 0 to 24%, as well as on the Na_2Cl_2 side. According to our data, the eutectic point is at 585° and 37.5% Na_2Cl_2 (Fig. 1, Table 1).

2) $PbCl_2$–PbI_2, which was studied by Monkemeier[3], forms a simple eutectic at 306° and 76% PbI_2. According to our data the liquidus curve has 3 branches: one for $PbCl_2$, one for the compound $PbCl_2 \cdot PbI_2$ which melts without decomposition with a maximum at 362° and 50% PbI_2, and one for PbI_2. The points of intersection lie at 360° and 42% PbI_2 and 334° and 73.5% PbI_2 (Fig. 1, Table 1).

3) PbI_2–Na_2I_2 was studied for the first time by us. The eutectic point is at 378° and 16.5% Na_2I_2 (Fig. 1, Table 1).

4) $PbCl_2$–Na_2Cl_2 was investigated by Treis [4]. A eutectic was found at 410° and 16.5% Na_2Cl_2 (Fig. 1).

Diagonal cross sections. The stable diagonal cross section PbI_2–Na_2Cl_2 (Fig. 1, Table 1) is a triangulating section with a saddle point eutectic at 380° and 8.5% Na_2Cl_2. It cuts across the PbI_2 and Na_2Cl_2 fields. The unstable diagonal cross section $PbCl_2$–Na_2I_2 (Fig. 1, Table 1) cuts across the $PbCl_2$, Na_2Cl_2 and Na_2I_2 fields at 393° and 13.5% Na_2I_2 and 556° and 74% Na_2I_2. The maximum at 658° on the Na_2Cl_2 branch is slightly displaced from the plane of the stable diagonal cross section and corresponds to 52.5% Na_2I_2. This indicates that an exchange equilibrium exists in the melts.

The crystallization surface of the reciprocal system. The reciprocal system investigated is similar to the Na, Cd ‖ Cl, I, system studied earlier [5]. A space diagram of system Na, Pb‖Cl, I was found by examining binary systems, diagonals, 11 internal cuts, and projections of simultaneous crystallization curves onto the plane of the polytherm of the binary system $PbCl_2$ - PbI_2.

TABLE 1

Binary Sides and Diagonal Cross Sections of Na, Pb ‖ Cl, I

PbI_2—Na_2I_2		$PbCl_2$—PbI_2		Na_2I_2—Na_2Cl_2		Diagonal		Diagonal	
% Na_2I_2	temperature	% PbI_2	temperature	% Na_2Cl_2	temperature	% Na_2I_2	temperature	% Na_2Cl_2	temperature
0.0	408°	0.0	496°	0.0	661°	0.0	496°	0.0	408°
5.0	402	5.0	473	10.0	646	2.5	488	2.5	397
10.0	389	10.0	454	15.0	638	5.0	468	5.0	387
15.0	382	20.0	422	20.0	626	7.5	443	7.5	382
17.5	386	30.0	396	25.0	613	10.0	418	10.0	413
20.0	402	35.0	380	30.0	602	12.5	388	15.0	489
22.5	419	40.0	365	32.5	599	15.0	417	20.0	534
25.0	437	45.0	360	35.0	592	17.5	453	25.0	565
27.5	457	50.0	362	37.5	587	20.0	486	30.0	592
						25.0	551		
30.0	473	55.0	361	40.0	592	30.0	603	35.0	616
32.5	490	60.0	360	45.0	611	35.0	630	40.0	633
						40.0	643		
35.0	508	65.0	355	50.0	631	45.0	653	45.0	647
						50.0	656		
40.0	540	67.5	349			55.0	656	50.0	660
						60.0	648		
42.5	553	70.0	344			65.0	626	55.0	670
						70.0	586		
45.0	564	72.5	336			75.0	563		
50.0	582	75.0	340			80.0	586		
55.0	590	80.0	358			82.5	604		

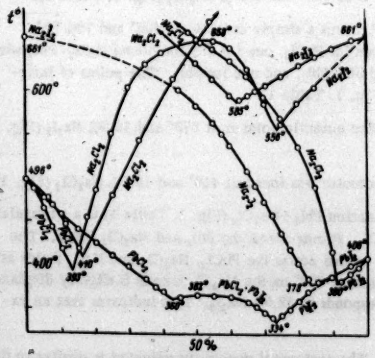

Fig. 1. Binary systems and diagonal cross sections of the reciprocal system Na, Pb ‖ Cl, I.

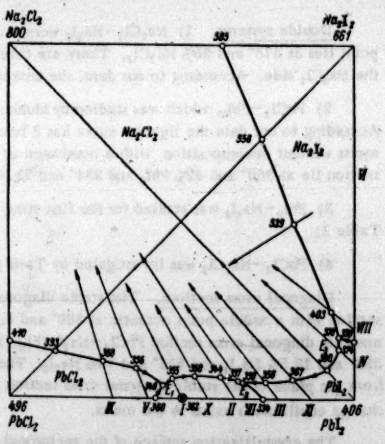

Fig. 2. Direction of inner cross sections of the reciprocal system Na, Pb ‖ Cl, I.

The directions of the eleven inner cross sections studied are given in Fig. 2. The composition of the initial mixture and the intersection points of the branches of the crystallization curves are given in Table 2. The crystallization curves of the mixtures (Fig. 3) are plotted on the basis of the data in Table 3. The projection of

TABLE 3

Inner Cross Sections

Cross section I		Cross section II		Cross section III		Cross section IV		Cross section V		Cross section VI		Cross section VII		Cross section VIII		Cross section IX		Cross section X		Cross section XI	
1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
0.0	362°	0.0	369°	0.0	377°	0.0	407°	0.0	375°	12.5	556°	0.0	355°	0.0	412°	0.0	399°	0.0	396°	0.0	377°
2.5	360	2.5	360	1.0	373	1.0	401	2.5	372	15.0	542	2.5	350	2.5	409	2.5	392	2.5	388	2.5	372
5.0	358	5.0	352	2.5	367	2.5	393	5.0	364	17.5	529	5.0	340	5.0	405	5.0	385	5.0	367	5.0	368
7.5	368	7.5	398	5.0	456	4.0	385	7.5	358	20.0	546	7.5	439	7.5	436	7.5	375	7.5	369	7.5	377
10.0	422	10.0	452	7.5	428	5.0	420	10.0	377	22.5	563	10.0	475	10.0	469	10.0	366	10.0	396	10.0	395
12.5	462	12.5	493	10.0	467	7.5	483	12.5	436	25.0	578	12.5	502	12.5	509	12.5	395	12.5	416	12.5	440
15.0	498	15.0	518	12.5	495	10.0	516	15.0	467	27.5	590	15.0	524	15.0	530	15.0	426	15.0	430	15.0	468
17.5	519	17.5	538	15.0	522	12.5	546	17.5	493	—	—	17.5	546	17.5	572	17.5	452	17.5	450	17.5	493
20.0	542	20.0	557	17.5	541	15.0	568	20.0	505	—	—	20.0	560	—	—	20.0	480	20.0	465	20.0	514
22.5	557	—	—	20.0	560	17.5	585	22.5	532	—	—									25.0	554
						20.0	600														

Note: 1st Column – percent of added component; 2nd column – temperature of the appearance of the first crystals.

TABLE 2

Table Summarizing the Inner Cross Sections of the Reciprocal System Na, Pb ‖ Cl, I

Test No.	Initial mixture of components	Branches of crystallization curves and their intersections				
		added component	branch 1	intersections 1 and 2: percent of added component	intersections 1 and 2: melting point	branch 2
I	50% $PbCl_2$ + 50% PbI_2	Na_2Cl_2	$PbCl_2 \cdot PbI_2$	6.5	355°	Na_2Cl_2
II	35% $PbCl_2$ + 65% PbI_2	Na_2Cl_2	$PbCl_2 \cdot PbI_2$	6.5	346	Na_2Cl_2
III	22.5% $PbCl_2$ + 77.5% PbI_2	Na_2Cl_2	PbI_2	5.0	356	Na_2Cl_2
IV	90% PbI_2 + 10% Na_2I_2	Na_2Cl_2	PbI_2	5.0	374	Na_2Cl_2
V	60% $PbCl_2$ + 40% PbI_2	Na_2Cl_2	$PbCl_2$	8.5	356	Na_2Cl_2
VI	40% PbI_2 + 60% Na_2I_2	$PbCl_2$	Na_2I_2	17.5	529	Na_2Cl_2
VII	30% $PbCl_2$ + 70% PbI_2	Na_2Cl_2	PbI_2	5.5	337	Na_2Cl_2
VIII	80% PbI_2 + 20% Na_2I_2	Na_2Cl_2	Na_2I_2	6.0	403	Na_2Cl_2
IX	70% $PbCl_2$ + 30% PbI_2	Na_2Cl_2	$PbCl_2$	10.5	368	Na_2Cl_2
X	42.5% $PbCl_2$ + 57.5% PbI_2	Na_2Cl_2	$PbCl_2 \cdot PbI_2$	6.5	350	Na_2Cl_2
XI	12.5% $PbCl_2$ + 87.5% PbI_2	Na_2Cl_2	PbI_2	6.0	367	Na_2Cl_2

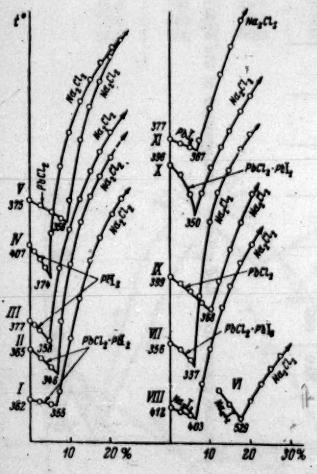

Fig. 3. Inner cross sections of the reciprocal system Na, Pb ‖ Cl, I.

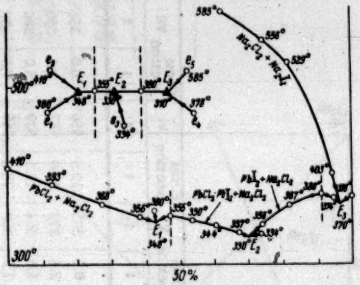

Fig. 4. Projection of the crystallization tree and plan of the crystallization tree of the reciprocal system Na, Pb ‖ Cl, I.

cocrystallization curves on the polythermal plane of the binary system $PbCl_2$–PbI_2 is given in Fig. 4.

The projections make it possible to determine more accurately the position of the triple invariant and isothermal points of the cocrystallization curves. The system is a semisingular irreversible reciprocal system with a subsidiary adiagonal. The composition of the invariant points and their equilibrium phases are given in Table 4.

The projection of the liquidus surfaces on the composition square is given in Fig. 5. The relative dimensions of the crystallization fields are given in Table 5.

TABLE 4

Point*	Temperature	Composition (in mole %)				Equilibrium phases
		$PbCl_2$	PbI_2	Na_2Cl_2	Na_2I_2	
E_1	348°	52.0	44.0	4.0	—	$PbCl_2$—Na_2Cl_2—$PbCl_2 \cdot PbI_2$
E_2	330	27.0	68.0	5.0	—	$PbCl_2 \cdot PbI_2$—Na_2Cl_2—PbI_2
E_3	370	—	82.5	5.0	12.5	PbI_2—Na_2Cl_2—Na_2I_2

*All three points are eutectic.

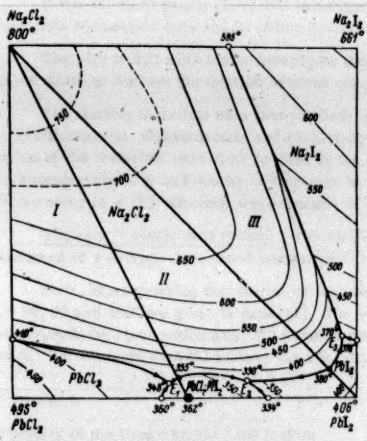

Fig. 5. Crystallization surface of the reciprocal system Na, Pb ‖ Cl, I.

TABLE 5

Crystallization field	Area (in %)
Lead chloride	5.54
Compound $PbCl_2 \cdot PbI_2$	1.75
Lead iodide	2.42
Sodium iodide	16.74
Sodium chloride	73.55

The triangulating diagonal cross section PbI_2—Na_2Cl_2 and adiagonal section $PbCl_2 \cdot PbI_2$—Na_2Cl_2 divide the system Na, Pb ‖ Cl, I into three phase triangles: 1) $PbCl_2 \cdot PbI_2$—Na_2Cl_2—$PbCl_2$, 2) $PbCl_2 \cdot PbI_2$—Na_2Cl_2—PbI_2, 3) PbI_2—Na_2Cl_2—Na_2I_2 (Fig. 5).

The compound $PbCl_2 \cdot PbI_2$ which melts without decomposition takes up a small area of 1.75 %. The effect of solvent shows the stability of this complex.

SUMMARY

1) The direction of reaction in the absence of a solvent in the irreversible reciprocal system with a subsidiary adiagonal is affected by the presence of the considerable heat effect of the exchange reaction (7.75 kcal per equiv.) and by the small heat effect from formation of the compound $PbCl_2 \cdot PbI_2$.

2) The fusion surface of the reciprocal system breaks up into five crystallization fields, one of which belongs to the compound $PbCl_2 \cdot PbI_2$, which melts without decomposition.

3) There are 3 triple eutectic and 2 double saddle points in the reciprocal system; the system is divided into 3 phase triangles (Fig. 5).

4) The exchange decomposition reaction is stronger than complex formation in the system.

LITERATURE CITED

[1] M. Amadori, Attireale acad. Lincei 22, 1, 467 (1912).

[2] Schobert, Dissertation (Leipzig, 1912).

[3] Technical Encyclopedia, Handbook of Physical, Chemical and Technical Values 6, 155.

[4] Treis, Neues Jahrb. Mineral. Geol. 37, 766 (1914).

[5] I. L. Ilyasov and A. G. Bergman, J. Gen. Chem. 26, 1288 (1956) (T. p. 1457).*

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INVESTIGATION OF THE DENSITY AND VISCOSITY OF BINARY SYSTEMS FORMED BY UREA WITH ACETIC ACID AND ITS CHLORO DERIVATIVES

Yu. I. Bokhovkina

It was shown in papers [1, 2] that investigation by physicochemical analysis of the binary systems, formed from urea with acetic acid and its chloro derivatives is of great practical and theoretical interest.

The aim of this work was to investigate the reaction of the components in the above binary systems in the liquid phase to find out the relation between composition and such measurable properties as density and viscosity.

The starting materials were first purified: acetic acid by freezing, urea by recrystallization from water, monochloroacetic, dichloroacetic and trichloroacetic acids by two distillations. After purification the melting points of the materials were close to those in the reference book [3]. The viscometer and pycnometer used for determining viscosity and density were placed in a water thermostat, whose temperature was kept constant with an accuracy of ± 0.1° viscosity was expressed in centipoises and concentration in molar percentage.

The urea – acetic acid system. The melting points of this system were investigated in papers [4-7]. The existence of a strongly dissociated compound $CO(NH_2)_2 \cdot 2CH_3COOH$ in it was established.

Data, characterizing the relation of viscosity and density to composition of the system $CO(NH_2)_2 - CH_3COOH$ at 80, 90 and 100° are given in paper [8]. The viscosity and density isotherms are smooth curves, slightly convex towards the composition axis. The compound given above probably dissociates completely at high temperatures. We therefore decided to carry out viscosity and density investigations at lower temperatures: 45, 60 and 70°.

TABLE 1

Viscosity of the Urea–Acetic Acid System

$CO(NH_2)_2$ content (mol.%)	Viscosity at the temperature		
	45°	60°	70°
5	0.968	0.685	0.586
10	1.344	0.883	0.724
15	1.859	1.161	0.904
20	2.595	1.494	1.149
25	3.480	1.904	1.429
30	4.635	2.44	1.760
35	5.902	2.968	2.122
40	7.328	3.565	2.519
45	—	4.183	2.960
50	—	—	3.392

TABLE 2

Density of the Urea–Acetic Acid System

$CO(NH_2)_2$ content (mol.%)	Density at the temperatures		
	45°	60°	70°
5	1.049	1.033	1.023
10	1.065	1.050	1.039
15	1.082	1.067	1.057
20	1.097	1.083	1.073
25	1.112	1.098	1.089
28	1.121	1.107	—
30	1.126	1.112	1.104
33	1.135	1.121	1.113
35	1.140	1.126	1.116
40	1.155	1.142	1.132
45	1.170	1.156	1.146
50	—	1.167	1.157

Mixtures containing up to 50% urea were investigated. The relations of viscosity to composition of the mixture are given in Table 1 and Fig. 1. The viscosity isotherms of the system are curves slightly convex towards the abscissa. The viscosity increases with a decrease in temperature as well as with an increase in urea concentration. Density data are given in Table 2. Curves of the relation of density to concentration are given in Fig. 1. They rise smoothly with increase in urea concentration.

The urea–monochloroacetic acid system. This system, whose melting points were determined [5] contains the compound $CO(NH_2)_2 \cdot 2CH_2ClCOOH$ which is dissociated to a large degree. The presence of the strongly dissociated compound $CO(NH_2)_2 \cdot CH_2ClCOOH$ was likewise established [1].

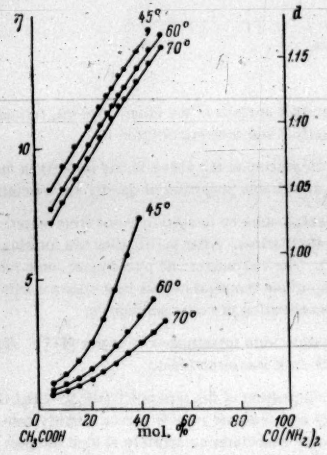

Fig. 1. Density (d) and viscosity (η) of the urea–acetic acid system.

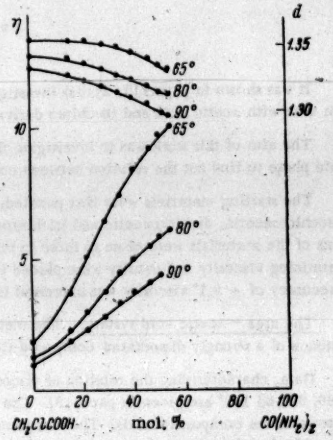

Fig. 2. Density (d) and viscosity (η) of the urea–monochloroacetic acid system.

Viscosity and density data for 80, 90 and 100° are given in [8]. The viscosity isotherms are curves, convex towards the composition axis. The curves of density against concentration bulge considerably away from the composition axis.

We investigated viscosity and density at 65, 80 and 90° (up to 55% urea) to check the existence of the compound detected in the melting-point diagram. Our data are different from those given in [8] in that we obtained higher values. The results of viscosity determination are given in Table 3 and in Fig. 2. All the viscosity isotherms rise sharply with an increase in urea content; with a small urea content they are slightly convex towards the composition axis, with a higher content they bulge away from the composition axis. The density isotherms (Table 4 and Fig. 2) bulge away from the composition axis.

The urea–dichloroacetic acid system. The presence of two compounds, $CO(NH_2)_2 \cdot 2CHCl_2COOH$ and $CO(NH_2)_2 \cdot CHCl_2COOH$, in this system, was established previously [1] by melting point determinations. We investigated the viscosity and density at 65, 70 and 75° (up to 62% urea).

As can be seen from the data in Table 5 and Fig. 3, the viscosity increases with an increase in urea content. At first the isotherms are somewhat convex towards the composition axis, but then they become strongly concave towards it, which indicates a stronger reaction of the components in this system than in the systems examined above, namely urea–acetic acid and urea–monochloroacetic acid.

Density data are given in Table 6 and Fig. 3.

TABLE 3

Viscosity of the Urea–Monochloroacetic Acid System

$CO(NH_2)_2$ content (mol.%)	Viscosity at the temperatures		
	65°	80°	90°
14.88	3.708	2.209	1.772
21.75	4.992	3.059	2.248
27.97	6.400	3.733	2.757
34.42	7.329	4.483	3.285
40.29	8.408	5.007	3.708
45.74	9.272	5.503	4.136
51.17	9.772	5.876	4.325
53.28	10.054	6.086	—

TABLE 4

Density of the Urea–Monochloroacetic Acid System

$CO(MH_2)_2$ content (mol.%)	Density at the temperatures		
	65°	80°	90°
0.0	1.356	1.343	1.335
14.88	1.355	1.341	1.328
21.70	1.355	1.336	1.325
27.97	1.352	1.332	1.320
34.42	1.350	1.328	1.315
40.29	1.345	1.324	1.310
45.74	1.340	1.319	1.306
51.17	1.335	1.314	1.299
53.28	1.333	1.313	1.298

TABLE 5

Viscosity of the Urea–Dichloroacetic Acid System

$CO(NH_2)_2$ content (mol.%)	Viscosity at the temperatures		
	65°	70°	75°
0.0	1.872	1.681	1.504
4.19	2.389	2.110	1.852
8.26	3.120	2.672	2.324
12.06	4.110	3.376	2.550
19.26	6.295	5.029	4.207
27.50	9.747	7.072	5.926
34.95	11.065	8.970	7.371
41.74	12.783	10.338	8.604
47.95	14.008	11.426	9.362
53.65	14.801	12.144	9.989
58.90	15.305	12.674	10.411
60.89	15.558	12.542	10.341

TABLE 6

Density of the Urea–Dichloroacetic Acid System

$CO(NH_2)_2$ content (mol.%)	Density at the temperatures		
	65°	70°	75°
0.0	1.490	1.485	1.480
4.19	1.490	1.485	1.480
8.26	1.490	1.485	1.480
12.06	1.488	1.484	1.479
19.26	1.483	1.479	1.475
27.50	1.476	1.472	1.468
34.95	1.467	1.464	1.459
41.74	1.458	1.454	1.448
47.95	1.450	1.444	1.438
53.65	1.437	1.433	1.427
58.90	1.428	1.421	1.415
60.89	1.420	1.415	1.408

TABLE 7

Viscosity of the Urea–Trichloroacetic Acid System

$CO(NH_2)_2$ content (mol.%)	Viscosity at the temperatures		
	80°	85°	95°
0.0	1.989	1.660	1.362
12.53	4.578	3.971	2.804
21.23	8.753	6.848	4.821
27.09	11.860	8.912	6.560
32.47	14.655	11.248	7.737
40.52	18.903	14.325	9.408
47.59	21.768	16.413	10.943
53.87	20.714	16.137	10.763
59.47	18.953	14.196	9.446
64.49	16.454	12.185	—

TABLE 8

Density of the Urea–Trichloroacetic Acid System

$CO(NH_2)_2$ content (mol.%)	Density at the temperatures		
	80°	85°	95°
0.0	1.564	1.557	1.553
12.53	1.564	1.557	1.552
21.23	1.563	1.557	1.548
27.09	1.561	1.556	1.544
32.47	1.557	1.551	1.539
40.52	1.548	1.540	1.527
47.59	1.530	1.524	1.512
53.87	1.512	1.505	1.492
59.47	—	1.486	—
64.49	—	1.469	—

The urea–trichloroacetic acid system. The melting points of this system had been investigated previously [1]. A compound with the composition $CO(NH_2)_2 \cdot CCl_3COOH$ was detected in the system. Viscosity and density were investigated at 80, 85 and 90°. Curves were plotted up to 65% urea. As can be seen from the data in Table 7 and Fig. 4, with an increase in urea concentration the viscosity greatly increases and passes through a maximum at 50% $CO(NH_2)_2$. We assumed that the maximum in the viscosity isotherms corresponded to the formation of the compound mentioned above. Density data are given in Table 8 and in Fig. 4.

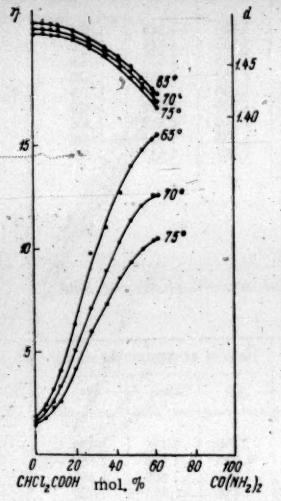

Fig. 3. Density (d) and viscosity (η) of the urea–dichloroacetic acid system.

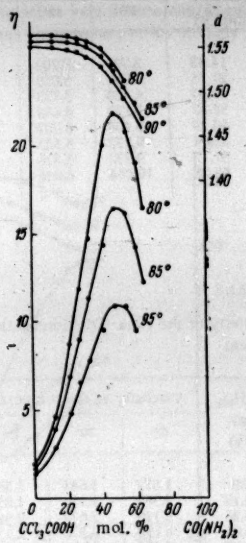

Fig. 4. Density (d) and viscosity (η) of the urea–trichloroacetic acid system.

DISCUSSION OF RESULTS

The viscosity of the binary systems urea–acetic acid, urea–monochloroacetic acid and urea–dichloroacetic acid changes monotonically with increase in urea content, without any characteristic breaks. It was also noted that as the number of chlorine atoms in the radical of the acetic acid increases, the convexity of the curves away from the composition axis increases; in the urea–acetic acid system the viscosity isotherms change almost additively, in the urea–dichloroacetic acid system, they bulge away from the composition axis considerably, while the curves in the urea–trichloroacetic acid system have an irrational maximum. This change in the character of the viscosity isotherms is caused by increased chemical reaction in the systems, owing to the increasing number of chlorine atoms in the radical of the acetic acid [9]. The irrational maximum in isotherms of the urea–trichloroacetic acid system shifts with a rise in temperature towards the more viscous urea. The maximum, which is at 50% urea, indicates the existence of the compound $CO(NH_2)_2 \cdot CCl_3COOH$, which was established by determination of the melting points.

The density isotherm curves which bulge away from the composition axis indicate some compression in the systems. Some authors [10] consider that this effect is caused by chemical reaction of the components, while others [11] consider that the compression may be due to other reasons. Therefore, the density isotherms should be examined only on the basis of other, more characteristic, properties. In our case the marked deviation of the density isotherms from additivity does, in a certain way, indicate chemical reaction.

SUMMARY

1) The density and viscosity of the binary systems urea–acetic acid, urea–monochloroacetic acid, urea–dichloroacetic acid and urea–trichloroacetic acid were investigated.

2) The density of the urea–acetic acid system changes almost additively and gives no indication of compound formation. In the urea–monochloroacetic acid, urea–dichloroacetic acid and urea–trichloroacetic acid systems, the density isotherms bulge away from the composition axis more with the increasing number of chlorine atoms in the acetic acid radical.

3) The viscosity isotherms in the urea–trichloroacetic acid system pass through a maximum which is due to the formation of the compound $CO(NH_2)_2 \cdot CCl_3COOH$.

4) It is impossible to decide on the existence of compounds in the liquid phase by the form of the viscosity isotherms in the urea–acetic acid, urea–monochloroacetic acid and urea–dichloroacetic acid systems.

5) The introduction of chlorine into the acetic acid radical causes an increase in the reaction between urea and chloro derivatives of acetic acid.

LITERATURE CITED

[1] I. M. Bokhovkin and Yu. I. Bokhovkina, Trans. Archangel Inst. Timber Technol. 15, 145 (1955).

[2] Yu. I. Bokhovina and I. M. Bokhovkin, J. Gen. Chem. 26, 1062 (1956) (T. p. 1207).*

[3] The Chemist's Handbook (State Chem. Press, 1951), Vol. 2.

[4] Kremann, Weber and Zlehner, Monatsch. 46, 193 (1926).

[5] Puschin and Rikowski, Bull. soc. chim. roy. Yougoslav. 3, 65 (1932).

[6] A. E. Vetrov, J. Gen. Chem. 7, 1093 (1937).

[7] A. G. Bergman and M. N. Kuznetsova, J. Gen. Chem. 9, 631 (1939).

[8] N. Z. Rudenko and D. E. Dionisyev, J. Gen. Chem. 23, 721 (1953) (T. p. 751).*

[9] A. I. Shatenshtein, Theory of Acids and Bases (State Chem. Press, 1949).

[10] E. V. Biron, J. Russ. Chem. Soc. 41, 569 (1909); 42, 167 (1910); 45, 1985 (1913); 45, 2002 (1913).

[11] M. A. Klochko and I. G. Grigoryev, Bull. Sect. Phys. Chem. Anal., Acad. Sci. USSR 21, 288 (1952); 21, 303 (1952); 21, 310 (1952).

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A PHYSICOCHEMICAL INVESTIGATION OF THE WATER – ACETIC ANHYDRIDE – DIOXANE SYSTEM

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The acetic anhydride–water system is one of the most thoroughly investigated binary liquid systems; its components, in the ratio 1:1, form a non-dissociating (into components) compound: acetic acid. This is shown by many of the system's properties which have been studied by various authors and generalized by one of us [1]; the properties characterize the system as a rational one. It can be looked on as consisting of two systems: 1) one close to normal: acetic anhydride–acetic acid and 2) one irrational: acetic acid – water. Both the components of the basic system are anomalous liquids: acetic anhydride, due to the interaction of dipoles, and water, due to its hydrogen bonds. When mixed, these anomalous liquids undergo "normalization" besides the chemical reaction, i. e. the molecular complexes decompose into simple molecules.

We studied this system as a triple system, the third component being dioxane – a substance which is completely miscible with acetic anhydride, water and their reaction product, acetic acid. This triple system was studied to find out if it were possible to determine the average molecular weights and dipole moments of solutions of binary systems in dioxane, as well as elucidation of its nature and comparison with the acetic anhydride–water–acetone system. We had previously investigated the latter to determine the effect of a third component, acetone, on the interrelations between its basic components [2].

We studied the following four properties of the system with acetone: viscosity (η), density (d), surface tension (δ) and refractive index (n_D) at 25 and 40°; we also measured the same properties for this system.

EXPERIMENTAL

The density was measured with a Regnault pycnometer of 5 ml capacity; the viscosity with an Ostwald capillary viscometer; the surface tension by the method of maximum pressure of bubble formation, as modified by P. A. Rebinder; the refractive index was determined on a universal laboratory refractometer (Abbe), with a thermostatic fitting. The starting materials were carefully purified. The water was distilled 3 times. The acetic anhydride was stood over dehydrated sodium acetate and also distilled over the same material at atmospheric pressure, close to 760 mm. For the work we took fractions with b. p. 138.8-139° (d_4^{25} 1.0737, n_D^{25} 1.3880).

The dioxane was dried for a long time over anhydrous calcium chloride and distilled; the middle fractions were again dried over metallic sodium for several days and over the same, it was distilled in the range 101-101.3° at normal pressure; d_4^{25} 1.0265, n_D^{25} 1.4204.

Let us first consider the values of these properties obtained for the binary systems outlining the triangle. For the basic binary system (water–acetic anhydride), we repeated the density and viscosity measurements, carried out by O. Faust [3], who did not report the individual points for the system, as well as N. S. Kurnakov's measurements [4]. N. S. Kurnakov initially gave only the character of the curves in a short note [4] and later gave diagrams of these properties without the numerical data [5]. We therefore consider it necessary to report the numerical values we obtained for viscosity and density at two temperatures (Table 1).

The density and viscosity isotherms, plotted from the data in Table 1, are in complete agreement with the isotherms given by N. S. Kurnakov.

TABLE 1

Density and Viscosity of the Water–Acetic Anhydride System

Amount of $(CH_3CO)_2O$ (in mol.%)	d_4^{25}	d_4^{40}	η (in centipoises) 25°	η (in centipoises) 40°	$\alpha = \frac{\eta_{t_1} - \eta_{t_2}}{t_2 - t_1}$
0	0.9965	0.9915	0.894	0.656	0.0158
20	1.0615	1.0485	2.189	1.484	0.0470
40	1.0565	1.0408	1.852	1.294	0.0372
45	1.0506	1.0348	1.497	1.104	0.0262
50	1.0452	1.0293	1.193	0.921	0.0181
60	1.0523	1.0354	1.059	0.835	0.0149
80	1.0642	1.0476	0.936	0.735	0.0134
100	1.0737	1.0557	0.842	0.693	0.0099

Within the limits of error of the methods used, the results of surface tension and refractive index measurements coincided with our previous data [2, 6].

Many of the properties of the dioxane–water system have been studied by a number of authors. Govorka et al. [7] and M. Z. Tsypin with one of us [8, 9] measured the density. Geddes [10] and M. Z. Tsypin [8, 9] studied the viscosity. The numerical values of these properties agree well with the data given by the authors mentioned. However, we considered it necessary to give them fully in Tables 2 and 3 as we obtained values for two temperatures, and this allows us to consider the temperature relation of these properties.

TABLE 2

Density and Viscosity of the Dioxane–Water System

Content (mol.%)	Content (vol. %)	d_4^{25}	d_4^{40}	Viscosity in centipoises η 25°	Viscosity in centipoises η 40°	Temperature coefficient α
0	0	0.9965	0.9915	0.894	0.656	0.0158
20	54.16	1.0343	1.0232	1.923	1.327	0.0397
40	75.92	1.0355	1.0233	1.784	1.273	0.0341
60	87.64	1.0314	1.0176	1.453	1.087	0.0244
80	94.96	1.0286	1.0137	1.262	1.957	0.0196
100	100	1.0265	1.0101	1.181	0.992	0.0174

The density and viscosity isotherms are curves with a maximum lying between 20 and 40 mol. % of dioxane and illustrate the irrational character of the system.

TABLE 3.

Surface Tension and Refractive Index of the Dioxane–Water System

Content $C_4H_8O_2$ (mol. %)	Content $C_4H_8O_2$ (mol.%)	$\sigma_{20°}$	$\sigma_{40°}$	$\gamma = \frac{\sigma_{t_1} - \sigma_{t_2}}{t_2 - t_1}$	n_D^{25}	n_D^{40}	Additive values	Deviation from additivity Δn
0	0	71.97	69.48	0.166	1.3325	1.3309	—	—
20	54.16	40.37	37.97	0.160	1.3869	1.3820	1.3800	+0.0069
40	75.92	36.81	35.06	0.117	1.4035	1.3978	1.3991	+0.0044
60	87.64	34.85	33.15	0.113	1.4127	1.4050	1.4095	+0.0032
80	94.96	33.86	31.95	0.127	1.4173	1.4095	1.4160	+0.0013
100	100	33.65	31.57	0.141	1.4204	1.4126	—	—

The deviations of the refractive indices from the additive values at 25° (expressing the composition in vol. %) are given in Table 3. The greatest deviation is in the range between 20 and 40 mol. % of dioxane.

TABLE 4

Density and Viscosity of the Water–Acetic Anhydride–Dioxane System

Sample No.	Content (mol. %)			d_4^{25}	d_4^{40}	Viscosity in centipoises	
	H_2O	$(CH_3CO)_2O$	$C_4H_8O_2$			η^{25}	η^{40}
1	64	16	20	1.0491	1.0352	2.179	1.498
2	48	32	20	1.0483	1.0343	1.752	1.268
3	40	40	20	1.0442	1.0285	1.332	1.012
4	32	48	20	1.0505	1.0336	1.169	0.909
5	16	64	20	1.0586	1.0423	0.986	0.784
6	48	12	40	1.0418	1.0264	1.750	1.242
7	36	24	40	1.0427	1.0277	1.561	1.153
8	30	30	40	1.0434	1.0268	1.333	1.013
9	24	36	40	1.0475	1.0302	1.203	0.938
10	12	48	40	1.0522	1.0355	1.023	0.809
11	32	8	60	1.0343	1.0184	1.427	1.059
12	24	16	60	1.0376	1.0215	1.352	1.023
13	20	20	60	1.0411	1.0245	1.285	0.981
14	16	24	60	1.0425	1.0267	1.196	0.924
15	8	32	60	1.0466	1.0289	1.063	0.833
16	16	4	80	1.0318	1.0160	1.236	0.941
17	12	8	80	1.0339	1.0173	1.214	0.928
18	10	10	80	1.0348	1.0185	1.187	0.920
19	8	12	80	1.0358	1.0197	1.153	0.896
20	4	16	80	1.0369	1.0208	1.089	0.835

The surface tension isotherms, plotted from the data in Table 3, are typical of binary systems with a surface-active component (in our case – dioxane) and do not reflect the chemical reaction, which is hidden by the adsorption of dioxane in the surface layer.

TABLE 5

Surface Tension and Refractive Index of the Water–Acetic Anhydride–Dioxane System

Sample No.	Content (mol. %)			σ^{25}	σ^{40}	n_D^{25}	n_D^{40}
	H_2O	$(CH_3CO)_2O$	$C_4H_8O_2$				
1	64	16	20	34.85	33.22	1.3910	1.3851
2	48	32	20	31.32	29.91	1.3883	1.3821
3	40	40	20	29.34	27.64	1.3853	1.3790
4	32	48	20	29.97	28.35	1.3874	1.3811
5	16	64	20	31.74	30.04	1.3916	1.3848
6	48	12	40	34.21	32.38	1.4021	1.3958
7	36	24	40	32.73	30.82	1.3985	1.3920
8	30	30	40	31.70	30.00	1.3973	1.3908
9	24	36	40	32.45	30.54	1.3980	1.3910
10	12	48	40	32.85	30.90	1.3995	1.3923
11	32	8	60	33.86	32.16	1.4100	1.4027
12	24	16	60	33.08	31.60	1.4076	1.4007
13	20	20	60	32.52	30.75	1.4068	1.4000
14	16	24	60	32.88	31.11	1.4067	1.3999
15	8	32	60	33.22	31.45	1.4063	1.3993
16	16	4	80	33.86	31.95	1.4159	1.4086
17	12	8	80	33.29	31.53	1.4149	1.4077
18	10	10	80	31.02	31.30	1.4145	1.4072
19	8	12	80	33.44	31.32	1.4140	1.4068
20	4	16	80	33.37	31.24	1.4134	1.4062

From a thorough investigation of this system by physicochemical analysis, M. Z. Tsypin and one of us [8, 9] came to the conclusion that a chemical reaction in the system leads to the formation of dioxane tetra- and dihydrates by hydrogen bonding, which are dissociated in solution.

Our data on the acetic anhydride–dioxane system [11] showed that the relations of the components with each other are close to normal. The viscosity isotherms are typical for systems in which there is decomposition of associated molecules of the original liquids during mutual solution. Apparently in this case also, the same effect may be observed to a slight degree and is reflected only in the curves for the viscosity, which is the most sensitive property.

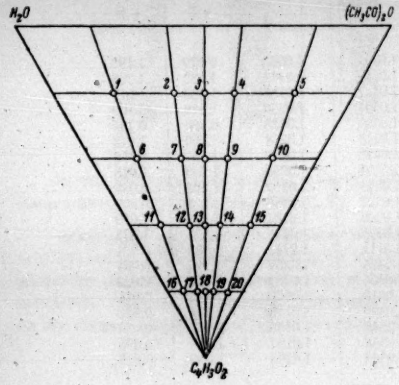

Fig. 1. Diagram of the compositions of the triple mixtures.

The Triple System Water – Acetic Anhydride – Dioxane

The results of measuring the properties in question for the triple system are given in Tables 4 and 5. Figure 1, which is a graphical illustration of the solutions referred to by number in Tables 4 and 5, shows that we took isoconcentrates, corresponding to 20, 40, 60 and 80 mol. % of dioxane.

Figures 2-4 are diagrams representing d, n_D, σ and η of the triple system at 25°. In their median section lie the isotherms corresponding to the properties of the derived binary system, acetic acid–dioxane, which show the irrational relations of its components, particularly in the viscosity and surface tension curves. The chemical reaction here may be explained by the formation of hydrogen bonds [11].

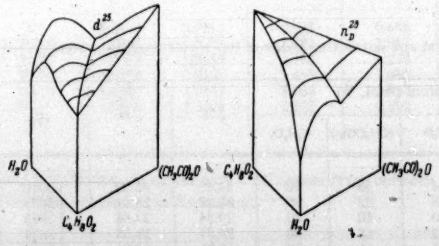

Fig. 2. Density and refractive index surfaces for the triple system water–acetic anhydride–dioxane.

The isothermal surfaces of all the properties of the triple system which we studied at 25° (also at 40°) consist of two separate surfaces of the subsidiary triple systems: water–acetic acid–dioxane and acetic acid–acetic anhydride–dioxane, intersecting in a singular syncline edge, corresponding to the isotherm of the acetic acid–water system.

Both the isothermal density surfaces (Fig. 2) bulge away from the composition triangle. The surface of the water–acetic acid system has a maximum, reflecting the chemical reaction of water with acetic acid and dioxane. The slight convexity of the isothermal density surface, corresponding to the acetic acid–acetic anhydride–dioxane system, indicates condensation, apparently due to reaction between dioxane and acetic acid [11].

The isothermal refractive index surface of the system is similar to that for density (Fig. 2), except that the maximum, corresponding to acetic acid monohydrate, does not stand out so much. The general character of the isothermal refractive index surface of the triple system studied is similar to that of the surface for the same property of the acetic anhydride–water–acetone system [2] and differs only in its disposition (in the first system the n_D surface rises towards dioxane and in the second it falls towards acetone). The σ surfaces of the triple systems water–acetic anhydride with dioxane and acetone are also similar. As in the system with acetone, the surface "falls" sharply from water to the other two components (i. e. in our case to acetic acid and dioxane) due to the high surface activity of acetic acid and dioxane in water and, being concave towards the water, it then bulges away from the composition triangle (Fig. 3).

The σ surface of the triple system acetic acid–acetic anhydride–dioxane bulges slightly, close to the isotherm of the acetic acid–dioxane system, and becomes linear as the solutions are diluted with acetic anhydride, which does not react chemically either with acetic acid or with dioxane.

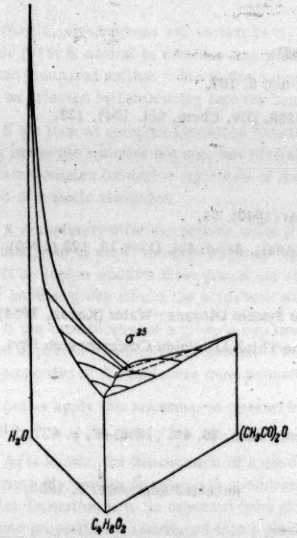

Fig. 3. Surface tension surface of the triple system water–acetic anhydride–dioxane.

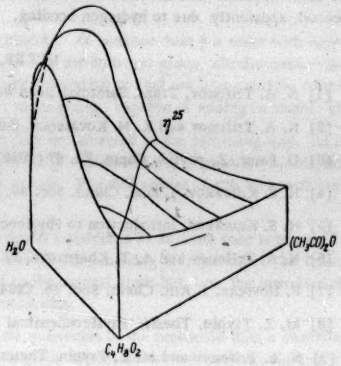

Fig. 4. Viscosity surface of the triple system water–acetic anhydride–dioxane.

From the data on the viscosity of the acetic anhydride–water system, it follows that it has an isotherm with a point where the branches meet; this mean Kurnakov point * corresponds to the acetic acid formed in the system.

By diluting this system with dioxane, we obtained an isothermal surface for the viscosity of the triple system, which, as in the cases of the other properties, consists of two parts intersecting in an edge, which corresponds to the isotherm of the subsidiary acetic acid–dioxane system (Fig. 4). The angle at which the two branches of the isoconcentrates meet becomes more obtuse as the dioxane concentration in the solutions increases (from 20 to 80 mol.%), i. e. it is as if the unusual character of the η (c) isotherm of the original binary system is smoothed out. The maximum on the η surface of the subsidiary water–acetic acid–dioxane system, the components of which all react together chemically, gradually becomes slightly convex close to the dioxane ordinate.

The η surface of the second subsidiary system (acetic anhydride–acetic acid–dioxane) is convex to the plane of the composition triangle in the region close to the isotherm of the acetic acid–dioxane system and is concave in the remaining part.

*Using the terminology proposed by one of us.

SUMMARY

1) The density, viscosity, surface tension and refractive index of the water–acetic anhydride–dioxane system were studied at 25 and 40°. It was shown that the introduction of a third component into the rational system, water–acetic anhydride, did not eliminate its singular character.

The isothermal surfaces of the properties studied for the system consisted of two separate surfaces, which intersected at a syncline edge corresponding to solutions of the acetic acid–dioxane system.

2) We have reproduced data, obtained previously by other investigators, for the density, viscosity, surface tension and refractive index of the systems acetic anhydride–water and dioxane–water, which outline the triple system (and σ and n_D were also studied at two temperatures for the second system).

3) For the first time d, η, σ and n_D were measured for the binary systems acetic anhydride–dioxane and acetic acid–dioxane. It was shown that there is no chemical reaction in the first system, but that there is in the second, apparently due to hydrogen bonding.

LITERATURE CITED

[1] N. A. Trifonov, Trans. Saratovsk Road Inst. 1939, Collection 5, 167.

[2] N. A. Trifonov and K. N. Kovalenko, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1947, 153.

[3] O. Faust, Z. physik. Chem. 79, 97 (1912).

[4] N. S. Kurnakov, J. Russ. Chem. Soc. 50, 157 (1918).

[5] N. S. Kurnakov, Introduction to Physicochemical Analysis (1940), 51.

[6] N. A. Trifonov and A. T. Khalezova, Bull. Sect. Chem. Anal., Acad. Sci. USSR 12, 123 (1940).

[7] F. Hovorka, J. Am. Chem. Soc. 58, 2264 (1936).

[8] M. Z. Tsypin, Thesis: Physicochemical Properties of the System Dioxane–Water (Kazan, 1954).

[9] N. A. Trifonov and M. Z. Tsypin, Theses of Reports of the Third All-Union Conference on Phys.-Chem. Analysis (Moscow, 1955), 161.

[10] A. Geddes, J. Am. Chem. Soc. 55, 4832 (1933).

[11] K. N. Kovalenko, N. A. Trifonov and D. S. Tissen, J. Gen. Chem. 26, 403 (1956) (T. p. 427).*

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*T. p. = C. B. Translation pagination.

THE FORMATION OF COMPLEXES BY STANNIC CHLORIDE WITH SOME PHENOL DERIVATIVES

M. Usanovich and E. Pichugina

Phenol, nitrobenzene and aniline [1-5] add to stannic chloride. As benzene does not react with stannic chloride [6] it is natural to consider that phenol adds to $SnCl_4$ due to the hydroxyl group, nitrobenzene – due to the nitro group, and aniline – due to the amino group. It seemed interesting to find out how complex formation would be affected by introducing into the banzene ring two or more groups, capable of adding to stannic chloride.

If we look at complex formation formally, the question may be answered in the following way. As the adding molecule contains not one, but several groups, due to which it can add to the central atom, this should facilitate complex formation regardless of the nature of these groups. The difficulties of this approach could only be of a steric character.

A completely different picture arises if complex formation is considered as an acid-base reaction [7-9]. From this point of view, the type of group that is introduced into the benzene ring is important. The important factor is no longer whether these groups are capable of adding to the central atom, but how the introduction of one or another group affects the acid-base properties of the molecules.

If the introduction of a given group strengthens the acidic properties of the molecule then a negative effect may be expected in complex formation. The introduction of a group which, on the contrary, strengthens the basic properties of the molecule must promote complex formation.

Let us apply this reasoning to systems in which the addendum is phenol or one of its nitro and amino derivatives.

As is known, the introduction of a nitro group into a phenol molecule strengthens the acidic properties of the latter. If complex formation is considered as an acid-base reaction then a decrease in the capacity for complex formation is to be expected from phenol to picric acid. However, if an amino group, which strengthens the basic properties, is introduced into a phenol molecule, then we should expect that the aminophenol would add to stannic chloride more readily than phenol. If, however, the effect of the acid-base properties of the addendum on complex formation is not considered, then the introduction of either a nitro group or an amino group into a phenol molecule would facilitate complex formation (of course, if no steric hindrances and thus created).

We studied the systems formed by stannic chloride with o- and p-nitrophenol, 2,4-dinitrophenol and p-aminophenol to determine which of these two points of view on complex formation is the correct one.

EXPERIMENTAL

The system $SnCl_4$–o-$C_6H_4(NO_2)OH$. The results of viscosity and density measurements at 25, 40 and 60° are given in Tables 1 and 2.

The viscosity isotherms (Fig. 1) have the same shape at all temperatures and curve away from the composition axis. The viscosity isotherm for 25° was determined only up to 50 mol. % of o-nitrophenol as mixtures containing greater amounts of nitrophenol crystallized at this temperature. The relation of the temperature coefficient of viscosity B to composition is shown in Fig. 2. The values of B were calculated by an exponential formula.

The temperature coefficient changed linearly with changes in composition. The specific volume isotherms (Fig. 3) were also straight lines. The components of the system and their mixtures were electrically nonconducting.

The data obtained did not indicate chemical reaction.

The system $SnCl_4$–p-$C_6H_4(NO_2)OH$ gave liquid phases, which separated into layers and so its melting points only were examined.

Mixtures containing from 6 to 58 mol. % of p-nitrophenol separated into layers. The cooling curves of mixtures of this composition showed only one break lying below the temperature of separation into layers and corresponding to a monotectic transition.

TABLE 1

$C_6H_4(NO_2)OH$ content (mol. %)	Viscosity (in centipoises)			B (cal.)
	25°	40°	60°	
0.00	0.881	0.758	0.637	1788
19.86	1.06	0.881	0.719	2100
50.82	1.75	1.32	0.980	3071
70.82	—	1.82	1.25	3681
94.69	—	2.62	—	—
95.21	—	—	1.78	4195
100.00	—	3.02	1.96	4440

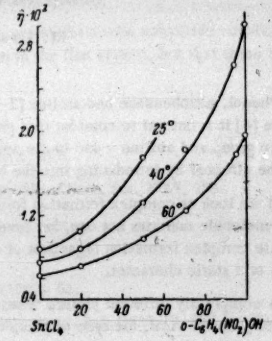

Fig. 1. Viscosity of the system stannic chloride–o-nitrophenol.

The cooling curves of mixtures containing more than 58 mol. % of p-nitrophenol showed two breaks. The temperature of the first break corresponded to the beginning of crystallization and that of the second to a monotectic transition.

Mixtures containing less than 6 mol. % of p-nitrophenol did not separate into layers and their cooling curves had only one break, corresponding to the beginning of crystallization (Table 3 and Fig. 4).

The p-nitrophenol crystallization line went up to almost 99 mol. % of $SnCl_4$ and between 6 and 58 mol. % of nitrophenol it crossed the region of separation into layers.

We did not determine the eutectic points as stannic chloride freezes at −33° and we did not go down to this temperature. We therefore did not determine the composition of the eutectic which lies very close to $SnCl_4$.

The region of separation into layers is contained in the curve ABC (Fig. 4) and above this complete miscibility was observed.

The system $SnCl_4$–2,4-$C_6H_3(NO_2)_2OH$. The cooling curves for all mixtures showed only one temperature break, corresponding to the beginning of crystallization.

The melting point diagram (Fig. 5) is of the simplest type with a single eutectic. As the crystallization line of the nitro compound went up to almost 99 mol. % of $SnCl_4$, we did not determine the eutectic composition or the eutectic point for the same reason as with the previous system. The melting point diagram did not show any reaction of the components.

We could not study the liquid phase of this system as the melting point of 2,4-dinitrophenol is close to the boiling point of stannic chloride.

The system $SnCl_4$–p-$C_6H_4(NH_2)OH$. Reaction did not occur on directly mixing stannic chloride with p-aminophenol as the latter did not dissolve in stannic chloride even on heating to the boiling point of stannic chloride. Therefore we decided to try to prepare the compound of stannic chloride and p-aminophenol from solution. Xylene was used as solvent as the p-aminophenol dissolved in it on heating.

TABLE 2

$SnCl_4$–o-$C_6H_4(NO_2)OH$

$C_6H_4(NO_2)OH$ content (weight %)	Density		
	25°	40°	60°
0.00	2.2190	2.1819	2.1288
11.60	2.0731	2.0370	1.9840
35.50	1.8050	1.7620	1.7243
56.39	—	1.5930	1.5500
90.44	—	1.3610	—
91.24	—	—	1.3265
100.00	—	1.3000	1.2750

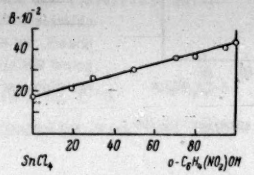

Fig. 2. Relation of the temperature coefficient of viscosity B to composition.

TABLE 3

$SnCl_4$–p-$C_6H_4(NO_2)OH$

$C_6H_4(NO_2)OH$ content (mol. %)	Temperature break		Temperature of separation into layers	$C_6H_4(NO_2)OH$ content (mol. %)	Temperature break		Temperature of separation into layers
	first	second			first	second	
2.6	66.0°	—	—	61.1	91.0°	86.0°	—
3.7	77.0	—	—	63.8	90.5	86.0	—
6.9	88.0	—	95.0	65.1	91.5	86.0	—
10.1	88.5	—	102.0	70.7	95.5	87.0	—
11.7	88.0	—		74.4	98.5	86.5	—
24.8	87.0	—	110.0	76.4	99.0	87.0	—
36.6	87.5	—	111.0	80.2	100.5	86.0	—
45.9	88.5	—	108.0	83.4	104.5	84.0	—
48.7	87.5	—		92.9	109.0	85.0	—
52.9	89.0	—	104.0	100.0	113.5	—	—
59.6	89.0	87.0	89.0				

On mixing xylene solutions of p-aminophenol and stannic chloride, a fine crystalline, lilac-colored precipitate came out.

Mixtures were prepared with ratios of 1 and 2 moles of aminophenol to 1 mole of stannic chloride. The precipitate was filtered off and washed with hot xylene.

The analytical results for the precipitates from mixing stannic chloride with p-aminophenol are as follows:

Amount of material (in g)	SnO_2 obtained (in g)	Sn found (in %)	Compound	Sn calculated (in %)
		1 mole of $SnCl_4$ to 2 moles of $C_6H_4(NH_2)OH$		
0.2219	0.0684	24.26	$SnCl_4 \cdot 2C_6H_4(NH_2)OH$	24.84
0.2280	0.0699	24.10		
		1 mole of $SnCl_4$ to 1 mole of $C_6H_4(NH_2)OH$		
0.2112	0.0643	24.00	$SnCl_4 \cdot C_6H_4(NH_2)OH$	32.14
0.2008	0.0628	24.62		

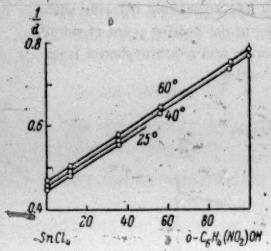

Fig. 3. Relation of specific volume to composition.

It is obvious from the analytical data that mixing stannic chloride with p-aminophenol in different ratios gives only one compound which has the composition $SnCl_4 \cdot 2C_6H_4(NH_2)OH$. This compound melts with decomposition at 224-225°.

DISCUSSION OF RESULTS

As a result of an examination of the systems formed by stannic chloride with o- and p-nitrophenol, 2,4-dinitrophenol and p-aminophenol, we established that stannic chloride forms a crystalline compound $SnCl_4 \cdot 2C_6H_4(NH_2)OH$ only with p-aminophenol. No chemical reaction was found between the components of the other systems.

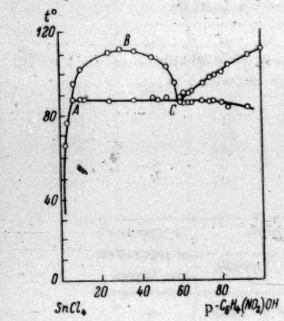

Fig. 4. Melting point diagram for the system stannic chloride–p-aminophenol.

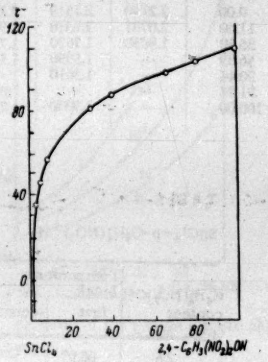

Fig. 5. Melting point diagram for the system stannic chloride–2,4-dinitrophenol.

The absence of a reaction between $SnCl_4$ and $o\text{-}C_6H_4(NO_2)OH$ may be due to the presence of a hydrogen bond between the hydroxyl group hydrogen and the nitro group oxygen, which are adjacent. The effect of an intramolecular hydrogen bond on complex formation is excluded in the case of p-nitrophenol. Due to the formation of layers in this system we could not arrive at a definite conclusion on the absence of reaction in it. Stannic chloride does not, apparently, react with 2,4-dinitrophenol, which may be explained by an increase in the acid properties of the dinitrophenol molecules due to the accumulation of nitro groups. In this case the absence of reaction can hardly be caused by steric hindrances.

Thus, the introduction of one or two NO_2 groups [2], an OH group [1] and an NH_2 group [4, 5] alone or together or NO_2 and OCH_3 groups [10] into a benzene molecule, with which $SnCl_4$ will not react, makes it capable of adding to $SnCl_4$. If, however, both OH and NO_2 groups are present in the benzene ring, they prevent the molecule from adding to $SnCl_4$. The reason for this cannot be steric hinderance, as dinitrobenzene, nitroanisole and aminophenol molecules add to $SnCl_4$.

All of these facts may be understood only if complex formation is considered as an acid-base reaction. Consequently, the data obtained by us confirm the point of view that complex formation should be considered an acid-base reaction.

SUMMARY

1) The viscosity and the density of the system $SnCl_4$–$o\text{-}C_6H_4(NO_2)OH$ was studied at 25, 40 and 60°.

2) Melting points were determined for the systems formed by $SnCl_4$ with $p\text{-}C_6H_4(NO_2)OH$ and $2,4\text{-}C_6H_3(NO_2)_2OH$.

3) A compound was obtained from stannic chloride with p-aminophenol with the composition $SnCl_4 \cdot 2C_6H_4(NH_2)OH$, which melted with decomposition at 224-225°.

LITERATURE CITED

[1] M. Usanovich and E. Pichugina, J. Gen. Chem. 26, 2125 (1956) (T. p. 2371)*

[2] M. Usanovich and E. Pichugina, J. Gen. Chem. 26, 2130 (1956) (T. p. 2377)*

[3] F. deCarli, Chem. Zentr. 1930, 1, 1280.

[4] W. Hieber and R. Wagner, Chem. Zentr. 1926, 1, 58.

[5] M. I. Usanovich, News Acad. Sci. Kazakh SSR 1950, No. 1, 73.

[6] N. S. Kurnakov, Collection of Selected Works (United Sci.-Tech. Press, 1938), Vol. I, p. 320.

[7] M. Usanovich, J. Gen. Chem. 9, 182 (1939).

[8] M. I. Usanovich, Bull. Acad. Sci. Kazakh SSR 1949, No. 3, 3.

[9] M. I. Usanovich, What are Acids and Bases (Acad. Sci. Kazakh SSR Press, 1953).

[10] N. A. Pushin, J. Gen. Chem. 18, 1599 (1948).

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*T. p. = C. B. Translation pagination.

THE VISCOSITY AND DENSITY OF THE STANNIC CHLORIDE – ANISOLE SYSTEM

M. Usanovich and E. Pichugina

Stannic chloride enters into a chemical reaction with phenol [1] in which stannic chloride acts as an acid while phenol acts as a base. We considered that it would be of interest to find out how the reaction with stannic chloride would be affected when the hydrogen in the phenol hydroxyl group was substituted by an aliphatic radical. For this we studied the system formed by stannic chloride with anisole. No noticeable heat effect was observed on mixing stannic chloride with anisole. The solutions obtained by mixing the colorless components were bright yellow color. No electroconductivity was observed in the system.

The viscosity and the density of the system were studied at 20, 40, 60 and 80°. The results of viscosity and density measurements are given in Tables 1 and 2. At 20° the viscosity curve (Fig. 1) goes through a flat maximum in the region of 90 mole % anisole. With increasing temperature the maximum shifts towards stannic chloride, while a minimum appears on the viscosity curves and, with increasing temperature, shifts towards anisole.

It is known that in the case of the formation of a partially dissociating compound in a system, the viscosity curve maximum, as a rule, shifts with increasing temperature towards the more viscous components. As already mentioned, the maximum in the diagram obtained by us shifts towards stannic chloride whose viscosity is less than that of anisole at 20 and 40°. The apparent contradiction of the general rule on the shift of the viscosity maxima is explained in this system by the greater viscosity temperature coefficient of anisole than that of stannic chloride and as a result stannic chloride becomes even more viscose than anisole at 60 and 80°.

TABLE 1

$C_6H_5OCH_3$	Viscosity (in centipoises)				Temperature coefficient of viscosity (B)
	20°	40°	60°	80°	
0.00	0.927	0.758	0.637	0.540	1836
29.95	0.932	0.724	0.590	0.501	2204
46.05	0.958	0.732	0.589	0.492	2380
59.82	1.01	0.746	0.593	0.491	2606
65.99	1.04	0.765	0.606	0.492	2667
72.50	1.07	0.779	0.626	0.502	2719
89.98	1.10	0.811	0.631	0.513	2764
100.00	1.08	0.795	0.627	0.502	2778

The specific volume isotherms (Fig. 2) are straight lines and this indicates the absence of either compression or expansion during the mixing of stannic chloride with anisole.

The viscosity isotherms obtained could be considered as indicating that stannic chloride reacts chemically with anisole with the formation of a compound which partially dissociates into its components. The appearance of a yellow color when the colorless components are mixed also indicates a reaction.

TABLE 2

$C_6H_5OCH_3$ (weight%)	Density			
	20°	40°	60°	80°
0.00	2.2340	2.1819	2.1288	2.0790
15.06	1.8911	1.8461	1.8069	1.7649
26.15	1.6955	1.6566	1.6213	1.5864
38.18	1.5269	1.4923	1.4608	1.4264
44.60	1.4493	1.4182	1.3860	1.3480
52.25	1.3655	1.3334	1.3049	1.2757
78.84	1.1314	1.1110	1.0885	1.0681
100.00	0.9978	0.9765	0.9588	0.9389

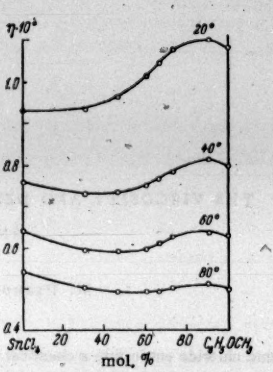

Fig. 1. Relation of viscosity to composition.

As the irrational maximum does not indicate the composition of the compound formed, we plotted a graph of the viscosity temperature coefficient (calculated according to an exponential formula) against composition (Fig. 3). This relation is expressed by a curve, concave towards the composition axis which implies a reaction between $SnCl_4$ and $C_6H_5OCH_3$, but likewise does not indicate the composition of the compound formed. We calculated the deviation of the curve obtained from the additive straight line and found that the maximum deviation is at a composition of $SnCl_4 \cdot 2C_6H_5OCH_3$.

Considering that anisole may add to $SnCl_4$ only by the oxygen, and that $SnCl_4$ has two free coordination positions, it is probable that the compound formed does have precisely such a composition. The absence of electroconductivity in the system also supports such a composition for the compound formed.

In comparing the two systems of stannic chloride–phenol and stannic chloride–anisole, it should be noted that chemical reaction has been observed in both systems.

Stannic chloride forms complexes with phenol, the same as with anisole, which are partially dissociated into the components. However, the system with phenol is characterized by electroconductivity, while the system with anisole does not transmit current. This difference is due to the fact that the compound formed in accor-

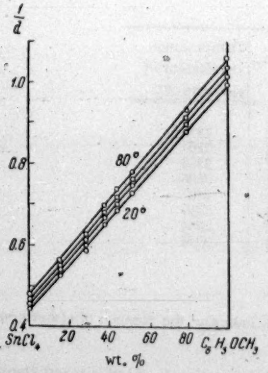

Fig. 2. The relation of specific volume to composition.

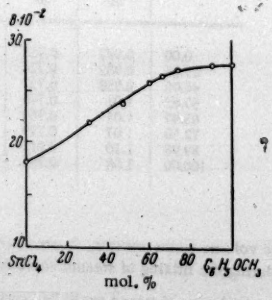

Fig. 3. The relation of viscosity temperature coefficient to composition.

dance with the coordination number Sn^{4+} in the $SnCl_4-C_6H_5OH$ system enters into a further acid-base reaction with the free phenol molecules with the formation of a salt-like product according to the reaction:

$$[SnCl_4(C_6H_5O)_2]H_2 + 2C_6H_5OH \rightleftharpoons [SnCl_4(C_6H_5O)_2]^{--} + 2C_6H_5OH_2^+.$$

The reaction of stannic chloride with anisole is restricted to the addition of 2 anisole molecules to one stannic chloride molecule. Compounds of such composition are not electrolytes.

Thus, a comparison of the systems formed by stannic chloride with phenol and with anisole, shows that the substitution of a CH_3 radical for the hydrogen in the phenol hydroxyl group, results in a compound of stannic chloride with anisole which does not show acid properties towards the excess anisole molecules, as is the case in the system with phenol.

SUMMARY

1) The viscosity and density of the $SnCl_4-C_6H_5OCH_3$ system were studied at 20, 40, 60 and 80°.

2) A hypothesis was put forward that the compound formed has the composition $SnCl_4 \cdot 2C_6H_5OCH_3$.

LITERATURE CITED

[1] M. Usanovich and E. Pichugina, J. Gen. Chem. 26, 2410 (1956) (T. p. 2691)*

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*T. p. = C. B. Translation pagination.

INVESTIGATION OF THE FIRST STAGES OF CATALYTIC CRACKING OF PARAFFINS ON ALUMINOSILICATE CATALYSTS BY THE EFFECT OF SMALL ADDITIVES ON THE PROCESS

T. L. Andrianova and S. Z. Roginsky

As catalytic cracking has a wide practical application, its mechanism and theory have been the subjects of numerous investigations which have uncovered a number of essential features of this complicated process. However, there is still no complete quantitative theory of the process. In particular, the nature of the active surface of the most important aluminosilicate catalysts and the character of the first stages of the process on this type of catalyst have not been fully elucidated. The latter problem may be elucidated by using suitable methods to investigate the effect of selected additives to the reacting hydrocarbon in the catalytic process. The materials which are especially interesting are those found in different stages of the system as intermediate active forms of precursors of these forms, as well as materials which, when absorbed by the surface, are capable of changing its acid-base and oxidation-reduction properties. The results of studying the first type of materials are given in this article. The following were investigated as such: olefins, to which are ascribed an important role in some cracking systems; alcohols, which easily generate olefins; simple ethers which according to literature data, form radicals on pyrolysis; as well as alkyl iodides, which are known to give free iodine; and also, possibly, iodine atoms and the corresponding radicals.

The experiments were carried out with n-octane in the usual flowing system at atmospheric pressure. Weighed quantities of the additives were introduced into the n-octane. The reaction products were frozen out in two traps by liquid nitrogen, and then, after freezing, the components, up to and including C_5, were fractionated at low temperature and analyzed chemically for unsaturated compounds. Liquid reaction products above C_6 were not analyzed due to their small amount and were considered as unreacted n-octane. The balance of the materials was calculated in each experiment. The experimental conditions were kept the same in all cases to obtain comparable results. The degree of conversion of n-octane alone and the total percentage conversion, including n-octane conversion plus the conversion of the additive, were compared in the different experiments; in this we considered that the additive underwent one hundred percent conversion under experimental conditions. For certain additives control experiments were carried out in which the character and degree of conversion of the given additive was established for its pure form on an aluminosilicate catalyst. Parallel control experiments were also carried out under the same conditions to establish the reproducibility of the results of n-octane cracking without additives. The results obtained on the effect of additives on n-octane cracking are given in the table. All the experiments were carried out under similar conditions: the experimental temperature was 518°, the volume (packed) of catalyst 75 ml, time of contact 8.5-11.1 seconds.

As can be seen from the table data, the addition of a small amount (about 0.1 mole %) of octylene increases n-octane cracking by 37.4% in comparison with pure n-octane cracking. Greater additions (2.64 mole %) either do not affect n-octane cracking or slightly inhibit it, as the exact degree of octylene conversion has not been determined accurately at the given partial pressure in a mixture with n-octane. This could be determined by using octylene labelled with C^{14}. Additions of approximately the same amount of alcohols (ethyl, n-octyl and n-cetyl) have an accelerating effect on n-octane cracking approximately of the same order as octylene. An addition of 0.1-0.42 mole % of n-butyl ether accelerates n-octane cracking by 35.9-31.8% respectively, a larger ether addition – 4.12% has less effect. The accelerating effect of alkyl halides on n-octane cracking increases

TABLE

Additive		Percent of conversion		Increase in cracking of n-octane itself due to the additive (in %)
name	mole %	total (including additive)	n-octane alone	
No additive	–	20.8 18.2	20.8 18.2 } 19.5*	–
Ethylene	0.17	26.3	26.2	26
Octylene	0.09	26.7	26.6	37.4
	0.27	25.0	24.8	27.2
	2.64	20.4	17.1	– 8.7**
Ethyl alcohol	0.16	26.9	26.8	37.4
	5.26	21.9	19.7	0
n-Octyl alcohol	0.17	24.7	24.2	23.8
n-Cetyl alcohol	0.1	26.2	26.0	33.4
	0.36	26.3	25.5	30.7
	0.78	23.8	22.2	13.0
n-Butyl ether	0.1	27.4	26.5	35.9
	0.42	26.4	25.7	31.8
	4.12	28.3	23.4	20.0
Ethyl iodide***	0.8	21.6	21.4	9.7
Octyl iodide	0.58	20.4	19.2	0
	4.11	30.4	26.8	37.5

*The yield of parallel experiments was ± 6-7 %.

**The decrease in n-octane cracking by 8.7 % due to the effect of 2.64% octylene arises from the supposition that is fully converted under these conditions.

***In calculating the total percent of conversion, including that of the alkyl halide additive, only the hydrocarbon part of the additive was considered as conversion was calculated according to products up to and including C_5, while the liquid products were considered as unreacted n-octane.

with increase in their concentration and it reaches 37.5% on adding 4.11 mole % of $C_8H_{17}I$. An experiment in which 4.15 mole % $C_8H_{17}I$ was added to n-octane, but without catalyst, showed that the acceleration of n-octane cracking due to the octyl iodide, could not have been caused by homogeneous catalysis. A control experiment on ethyl alcohol conversion on aluminosilicate at 506° and 0.4 seconds contact time showed that ethylene and water were formed and that the decomposition was 88.4%.

A control experiment on n-butyl ether conversion on aluminosilicate at 518° and 9.4 seconds contact time showed that 74.8% of the ether decomposed and that it formed various saturated and unsaturated hydrocarbons from C_1 to C_5 inclusive. Hydrocarbons with a greater number of carbon atoms were not analyzed.

The data given in the table show a noticeably similar accelerating effect of small concentrations of olefins and alcohols, which generate olefins. This fact points out the possibility of cracking starting with dehydrogenation. The decrease of the specific effect with increase of additive concentration seemed of interest. These facts can hardly be compatible with a simple single participation of olefins or alcohols in the catalytic process. This may be explained by a modification of the catalyst's surface by gaseous additives, or their participation in the formation of the initial centers for a surface chain reaction, for example, surface carbonium ions or surface radicals (semi radicals). The mechanism of the effect of ether is probably analogous. The nature of the effects we observed would be much clearer if they were studied at different temperatures and with labelled additives.

SUMMARY

1) Small additions of unsaturated hydrocarbons and alcohols (0.1-0.3 mole %) to n-octane increase its degree of conversion in cracking. An increase in the additives (to units of mole %) has a weaker or retarding effect on cracking.

2) The effect of n-butyl ether additions, is apparently similar to the effect of unsaturated hydrocarbons and alcohols.

3) Additions of alkyl iodides (of the order of 0.5 mole %) do not affect the degree of n-octane conversion; larger additions (of the order of 4 mole %) increase it.

4) The addition of halogen hydracids in concentrations up to 6 mole % to the hydrocarbon does not have any effect on n-octane cracking. A preliminary treatment of the catalyst with acid vapor had a slight positive effect.

5) The acceleration of n-octane cracking by the additives investigated shows that carbonium ions or radicals may act as active forms in the first stages of the process.

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INVESTIGATION OF THE CHEMICAL STRUCTURE OF DIVINYL THERMOPOLYMERS

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S. V. Lebedev established that the dimer ethenyl-1-cyclohexene-3 and two rubber-like polymers, only one of which was soluble in benzene, chloroform and carbon tetrachloride, were the thermopolymerization products of divinyl; he investigated the structure of the soluble divinyl thermopolymer by ozonization and found only succinaldehyde and succinic acid in the ozonolysis products. Both these products indicate that there are sections in the macromolecule of the divinyl thermopolymer which are formed by combination of divinyl molecules in the 1,4 position not less than two consecutive times in a row [1]. However, S. V. Lebedev does not state that the divinyl thermopolymer is formed by combination of divinyl molecules only in the 1,4-position. He wrote that "The structure of the polymer has not yet been established with certainty." At the same time, Harries wrote that the thermopolymer is formed by combination of divinyl molecules exclusively in the 1,4-position [2]. Such a polymer would be of great value explaining the relation between chemical structure and properties of polymers.

Polycarboxylic acids and their corresponding aldehyde acids and aldehydes, together with formic acid and formaldehyde, may be expected from ozonolysis of divinyl polymers which have units with inner and outer double bonds.*

The following objectives were set in this work: 1) to find out whether the divinyl thermopolymer is built up only from units with an inner double bond or whether it also contains units with outer bonds; 2) to establish the relative position of the units in the macromolecule of divinyl thermopolymers, and 3) to investigate the chemical structure of the divinyl thermopolymer which is insoluble in benzene, chloroform and carbon tetrachloride.

We investigated the chemical structure by ozonization of the soluble divinyl thermopolymer, obtained at 90°, and the insoluble one, obtained at 130°. The ozonization was carried out in ethyl acetate. The ozonides were decomposed by heating with water. The ozonide decomposition products were oxidized with a 1% aqueous solution of potassium permanganate; methyl esters were obtained from the acids with diazomethane. Formaldehyde, succinaldehyde and formic, succinic, butan-1,2,4-tricarboxylic and hexanetetracarboxylic acids were found in the ozonization products. The presence of formic acid and formaldehyde together with butan-1,2,4-tricarboxylic and hexanetetracarboxylic acids in the ozonolysis products indicates that the divinyl molecules combine in the 1,4- and 1,2-positions in the formation of divinyl thermopolymers. The ozonolysis results are given in Tables 1 and 2. It follows from data in Table 2 that the greater part of the carbon skeleton consists of divinyl molecules combined in the 1,4-position not less than two consecutive times. The section formed by combination of divinyl molecules in the 1,4−1,2−1,4-positions constitute a smaller percentage of the carbon skeleton. The sections having a 1,4−$(1,2)_2$−1,4 structure are even less developed. The structure of the insoluble thermopolymer (130°) does not differ from the structure of the soluble thermopolymer (90°). The results obtained show that the divinyl molecules combine in the 1,4- and 1,2-positions in divinyl thermopolymerization as in polymerization under different conditions [3, 4].

*Units with an inner double bond $-CH_2-CH=CH-CH_2-$ are formed by combination of divinyl molecules in the 1,4-position, while units with an outer double bond $-CH_2-\underset{\displaystyle CH=CH_2}{\underset{|}{CH}}-$ are formed by combination in the 1,2-position.

TABLE 1

Ozonolysis products	Percent of carbon skeleton of divinyl thermopolymer	
	soluble, obtained at 90°	insoluble, obtained at 130°
Succinic acid	45.6	43.7
Butan-1,2,4-tricarboxylic acid	13.8	14.8
Hexanetetracarboxylic acid	4.4	4.5

TABLE 2

Constitution of thermopolymer macromolecule sections	Percent of thermopolymer carbon skeleton in the section	
	soluble, obtained at 90°	insoluble, obtained at 130°
1,4−1,4	45.6	43.7
1,4−1,2−1,4	15.8*	17.0*
1,4−$(1,2)_2$−1,4	5.4*	5.4*

*The carbon in formic acid and formaldehyde, formed by ozonolysis of 1,2-units is considered in calculating the percent of carbon skeleton in the sections containing these bonds.

EXPERIMENTAL

The divinyl was prepared from divinyl tetrabromide, which had m. p. 115-116°, by treating it with zinc in a water-alcohol medium; it was dried with metallic sodium for 3 hours and distilled into a glass tube in which the polymerization was later carried out. For characterization, part of the divinyl was distilled on a Podbilnyak column at a pressure of 1500 mm. The boiling point of the pure divinyl at 760 mm was 4.5°. The distillation data completely satisfied the vapor pressure equation for divinyl [5]. There was neither head fraction nor residue on distillation.

The divinyl polymerization was carried out at 130° for 7 days and at 90° for 45 days. After polymerization, two layers were always found in tubes with thermolpolymers of divinyl: the upper was a colorless mobile liquid, which was a solution of polymer in divinyl, and the lower was a gelatin-like mass of insoluble polymer, saturated with divinyl dimer and soluble thermopolymer. The tubes were opened and the unpolymerized divinyl and its dimer were distilled off in vacuum, first at room temperature and then heated on a water bath. The divinyl and divinyl dimer were collected in a receiver cooled to − 80°. The dimer was completely separated from the polymer only in the last purification of the polymer. The soluble thermopolymer was separated from the insoluble polymer by the following method: the glass tubes in which the polymerization had been carried out, and from which the divinyl and its dimer had been distilled, were broken up and mixed with benzene. After 2-3 days the benzene-insoluble thermopolymer was filtered off from the benzene solution. The soluble thermopolymer was precipitated from benzene solution with ethyl alcohol and was finally purified by twice dissolving in benzene and reprecipitating with ethyl alcohol. The soluble thermopolymer remaining in the insoluble divinyl thermopolymer was extracted with benzene. The thermopolymers were dried to constant weight at 3-4 mm. All the work with divinyl thermopolymers was carried out under nitrogen. The soluble divinyl thermopolymer became insoluble after drying. Elementary composition of the soluble divinyl thermopolymer prepared at 90° (in %): C 88.78, 88.56; H 11.23, 11.17. Elementary composition of insoluble divinyl thermopolymer, prepared at 130° (in %): C 88.96, 89.03; H 11.20, 11.26. Calculated for $(C_4H_6)_x$ %: C 88.82; H 11.18.

12.7 g of soluble thermopolymer (90°) and 11.0 g of insoluble thermopolymer (130°) were ozonized in ethyl acetate at − 20°. The ozonization was considered complete when the concentration of ozone in the gas entering the reactor was practically the the same as the concentration of ozone in the gas coming out [6]. The ozonides formed dissolved in ethyl acetate and, after distilling off the solvent in vacuum at 20°, they appeared as colorless, viscous materials. The ozonides were decomposed with water by heating; the ozonolysis products were soluble in water. The aqueous solutions of the ozonolysis products were concentrated at 100 - 80 mm.

6.9 g of succinic acid was isolated from the concentrated aqueous solution of the ozonolysis products of the soluble divinyl thermopolymer (90°) and 4.1 g of succinic acid was isolated from the ozonolysis products of the insoluble divinyl thermopolymer (130°). After recrystallization from water, the succinic acid melted at 181-182° and an anhydride obtained from it melted at 119°

Found %: C 40.77; H 5.18. $C_4H_6O_4$. Calculated %: C 40.68; H 5.12.

TABLE 3

Fraction number	Products of ozonolysis of divinyl thermopolymers			
	soluble, prepared at 90°		insoluble, prepared at 130°	
	weight (in g)	n_D	weight (in g)	n_D^{20}
1	3.90	1.4168 (23°)	2.79	1.4181
2	2.54	1.4181 (22.5°)	4.60	1.4189
3	1.52	1.4300 (20°)	1.01	1.4330
4	2.91	1.4440 (20°)	2.98	1.4442
5	0.73	1.4474 (19°)	0.48	1.4471
6	0.69	1.4521 (19°)	–	–
7	0.62	1.4598 (19°)	1.16	1.4598

The aqueous distillate, obtained from the concentration of the ozonolysis products at 100-80 mm, contained succinaldehyde (pyrrole test) and a phenylhydrazone was prepared from it with m. p. 124°.

The ozonolysis products were oxidized by stirring with a 1% aqueous solution of potassium permanganate at 0°. After destroying excess potassium permanganate with sulfur dioxide, the manganese dioxide was filtered off and the filtrate was concentrated at 100 mm to a volume of 50 ml. The solution was acidified with phosphoric acid and extracted with ether to give carboxylic acids, from which methyl esters were distilled in vacuum from a flask with a pear fractionating column 19 cm high. At the end of the distillation, decomposition was observed, accompanied by the evolution of gas. The methyl esters given in Table 3 were isolated by the distillation. For fractions 1,2,4,5 and 7 we determined the elementary composition, molecular weight, equivalent weight and specific gravity. These determinations indicated that the 1st and 2nd fractions were dimethyl succinate, the 4th and 5th fractions were trimethyl butan-1,2,4-tricarboxylate and the 7th fraction was tetramethyl hexanetetracarboxylate. The properties of these esters are given in Tables 4, 5 and 6.

TABLE 4

Properties of Dimethyl Succinate Isolated from the Ozonolysis Products of Divinyl Thermopolymers *

Properties	Fraction No. (see Tab. 3)	From the ozonolysis products	
		of soluble divinyl thermopolymer, prepared at 90°	of insoluble divinyl thermopolymer, prepared at 130°
% C	2	49.34, 49.38	49.39, 49.05
% H	2	6.81, 6.97	6.88, 6.96
Molecular weight	1	147.42, 145.84	145.30
	2	146.63, 146.70	146.07, 145.78
Equivalent weight	1	71.98, 71.84	72.60, 73.23
	2	72.80, 74.24	72.00, 72.97
n_D	1	1.4168 (13°)	1.4181 (20°)
n_D	2	1.4181 (22.5°)	1.4189 (20°)
d_4	2	1.1192 (22.5°)	1.1197 (20°)

* Calculated for dimethyl succinate $C_6H_{10}O_4$ Calculated %: C 49.31; H 6.90. M 146.14; equivalent weight 73.07. Literature data: n_D^{20} 1.4192 [7], n_D^{183} 1.41986 [8], d_{15}^{15} 1.12611 [9], d_{25}^{25} 1.11718 [9], d_4^{20} 1.12077 [10].

TABLE 5

Properties of Trimethyl-1,2,4-Butanetricarboxylate Isolated from the Ozonolysis Products of Divinyl Thermopolymers *

Properties	Fraction No. (see Tab. 3)	From the ozonolysis products of soluble divinyl thermopolymer, prepared at 90°	From the ozonolysis products of insoluble divinyl thermopolymer, prepared at 130°
% C	4	51.83	51.30, 51.11
% C	5	52.46	—
% H	4	7.19	6.84, 6.82
% H	5	7.15	—
Molecular weight	4	232.36, 229.14	228.53, 228.84
	5	239.55	—
Equivalent weight	4	78.28, 78.40	78.37, 78.20
n_D^{20}	4	1.4440	1.4442
n_D^{20}	5	1.4474	—
d_4^{20}	4	1.1589	1.1636
MR_D	4	53.23	53.04

* Calculated for trimethyl butane-1,2,4-tricarboxylate ($C_{10}H_{16}O_6$) %: C 51.72; H 6.95. M 232.23; equivalent weight 77.41; n_D^{20} 1.4446 [7].

TABLE 6

Properties of Tetramethyl Hexanetetracarboxylate Isolated From the Ozonolysis Products of Divinyl Thermopolymers*

Properties	Fraction No. (see Tab. 3)	From the ozonolysis products of soluble divinyl thermopolymer, prepared at 90°	From the ozonolysis products of insoluble divinyl thermopolymer, prepared at 130°
% C	7	52.50, 52.73	52.84, 53.08
% H	7	6.95, 6.87	6.83, 6.85
Molecular weight	7	320.45	—
Equivalent weight	7	—	79.69
n_D^{19}	7	1.4598	1.4598
d_4^{20}	7	—	1.1867
MR_D	7	—	73.44

* Calculated for tetramethyl hexanetetracarboxylate ($C_{14}H_{22}O_8$)%: C 52.82; H 6.91. N 318.32; equivalent weight 79.58; n_D^{20} 1.4643 [7].

In investigations of divinyl thermopolymers, the percentage of units with outer double bonds [11] was calculated from the amount of formic acid [12] and formaldehyde found in the product of their ozonolysis. In the soluble divinyl thermopolymer, prepared at 90°, 31.6% of the units were found to have outer double bonds and in the insoluble thermopolymer, prepared at 130°, 27%.

SUMMARY

1) The chemical structure of the soluble (90°) and insoluble (130°) divinyl thermopolymers was investigated by ozonolysis.

2) It was established that divinyl thermopolymers are constructed, like other divinyl polymers, from units with inner and outer double bonds.

3) It was established that there are sections in the macromolecules of divinyl thermopolymers, whose structure can be schematically expressed as: 1,4−1,4; 1,4−1,2−1,4; 1,4−$(1,2)_2$−1,4.

4) It was shown that the chemical structure of the samples of the soluble and the insoluble polymers studied is the same.

LITERATURE CITED

[1] S. V. Lebedev, J. Russ. Chem. Soc. 41, 1818 (1909); 42, 949 (1910); 43, 1124 (1911) Investigation in the Field of Diethylenic Hydrocarbon Polymerization (All-Union Special Planning Office, 1913); Life and Collected Works of S. V. Lebedev (Leningrad, 1938); Collection: Academician S. V. Lebedev (Moscow, 1954).

[2] Harries, Ann. 383, 157-227 (1911); Untersuchungen über die natürlichen und künstlichen Kautschukarten (Berlin, 1919).

[3] I. R. Hill and Lewis, Trans. Faraday Soc. 35, 1067, 1073 (1939).

[4] A. I. Yakubchik, Collection: Academician S. V. Lebedev (Acad. Sci. USSR Press, 1954), 197.

[5] K. P. Mishchenko and A. I. Gulyaeva, Trans. Exptl. Casting Lab. B 1, 105 (1933).

[6] A. I. Yakubchik and N. G. Kasatkina, J. Gen. Chem. 25, 1473 (1955) (T. p. 1419).*

[7] N. Rabjohn and C. E. Bryan, J. Am. Chem. Soc. 69, 314 (1947).

[8] Brül, J. prakt. Chem. (2) 50, 140 (1894).

[9] Perkin, J. Chem. Soc. 43, 516 (1884).

[10] Emery, Ber. 22, 3185 (1889).

[11] A. I. Yakubchik, A. A. Vasilyev and V. M. Zhabina, J. Appl. Chem. (USSR) 17, 107 (1944).

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*T. p. = C. B. Translation pagination.

THE MECHANISM OF HETEROGENEOUS CATALYTIC ISOMERIZATION OF HYDROCARBONS ON ACID CATALYSTS

III. THE MECHANISM OF RACEMIZATION OF CAMPHENE ON TITANIC ACID

G. A. Rudakov and M. M. Shestaeva

Camphene (I) is rapidly racemized on heating with acids. Racemization has likewise been observed during interconversions of camphene ⇌ isoborneol or its esters, which also take place in an acidic medium. Various schemes explaining racemization of (I) have been put forward. Most of the schemes explain the racemization by spatial regrouping of the camphenyl carbonium ion (II), formed from (I) by proton addition and the bornyl (or isobornyl) carbonium ion (III) formed from (II) as a result of Wagner regrouping. The regrouping of S. S. Nametkin [1-4] remained experimentally convincing up to now; therefore some investigators, including the author of this scheme, were inclined to consider that racemization of (I) proceeded only according to it [2]. Recently, Roberts and Yansey [5] refuted this hypothesis on the bases of distribution of radioactivity in the oxidation products of partially racemized 8-C^{14} -labelled camphene and established that racemization occurs as a result of two processes – Nametkin regrouping and regrouping without the transfer of the CH_3-group in ion (II). Although Roberts and Yansey determined the relation of the rate constants of these interconversions, the character of the process remained unclear, as the system given by these authors for this spatial regrouping of (II) without the transfer of the CH_3-group had not been checked experimentally.

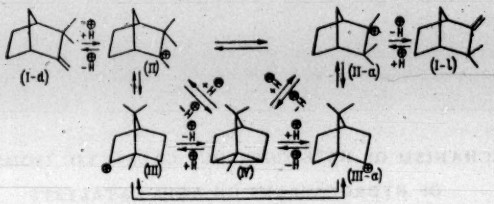
The so-called tricyclic system is the most singular of a number of proposed systems for racemization of (I). This system differs from all the rest in that according to this system, racemization does not occur due to spacial regrouping of ions (II) and (III) but as a result of reversible conversion of (I) into the tricyclene hydrocarbon (IV), which because of its symmetrical structure cannot have optical activity [6] and, consequently, is converted into racemic (I) during the reverse process.

(IV) was first considered as a necessary intermediate product in the conversion of camphene ⇌ isoborneol or its esters, but after Meerwein refuted such a course for the process, the tricyclic system was no longer considered probable. However, the possibility of racemization of (I) by tricyclic regrouping must be reconsidered as the works of Swann and Gripwell [8] prove the existence of a reversible equilibrium (I ⇌ IV) in the presence of a number of catalysts. Taking into account the occurence of simultaneous spatial regrouping of carbonium ions (II) and (III), recemization of (I) may be expressed by scheme 1.

The regroupings of Nametkin and Meerwein [9] were given conditionally in the system as the spatial regroupings of ions (II) and (III). The system would not change basically if other spatial regroupings of ions (II) and (III) were assumed to be proceeding simultaneously with the tricyclic regrouping. Formation of (IV) may also be indicated by the complex-ester mechanism. This also does not change the system basically.

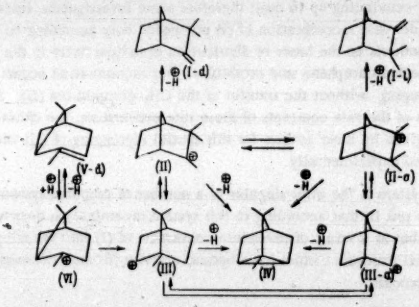
The present investigation aimed at a comparison of the rate of tricyclic regrouping with the rate of spatial regrouping of ions (II) and (III), so as to determine whether this regrouping plays a noticeable part in racemization of (I).

Scheme 1.



The existence of a whole series of reversible interconversions makes the solution of the problem exceedingly complicated. The authors solved it in the case of racemization of (I) by titanic acid. The fact, observed by the authors [10], that the reversible interconversions of ions (II) and (III) into (I) and (IV) become irreversible if the reaction is carried out in the presence of α-pinene (V), was used as the basis of the investigation method employed. A reaction mixture of the desired composition was readily obtained as (V) isomerizes when heated with titanic acid into (I) and (IV) and, furthermore, the ions (VI), (II) and (III) were intermediate products. The conversion of ions (VI), (II) and (III) obtained, for example, from optical active d-α-pinene, then appears as follows:

Scheme 2.



Under these conditions, due to the presence of excess (V) ions (II) and (III) are formed continuously and all the tricyclene formed from the ions (II) and (III) accumulates in the reaction products, and racemization occurs only as a result of spatial regroupings of (II) and (III). These latter regroupings have time to proceed only to an insignificant degree during the period that the ions (II) and (III) exist, and therefore they can also be considered irreversible.

It follows from the above that it is possible to find the relation between the rate constants for the racemization of (I): (k_1) as a result of the reversible conversion (I ⇌ IV), and (k_2) as a result of the spatial regroupings of (II) and (III), from the ratio:

$$\frac{k_1}{k_2} = \frac{P}{\Delta\alpha}, \qquad (1)$$

where P is the (IV) content in percent in the mixture of (I) and (IV) formed during the reaction, $\Delta\alpha$ is the difference between calculated camphene and that actually obtained by specific rotation expressed in percentage. The latter value was determined from the equation:

$$\Delta\alpha = \frac{\left(\frac{118.5 \cdot a}{50.6} - b\right) \cdot 100}{\frac{118.5 \cdot a}{50.6}}, \qquad (2)$$

where 118.5 is the most reliable value of $[\alpha]_D$ for optically pure camphene (in benzene) [11, 12], 50.6 is the most reliable value of $[\alpha]_D$ for optically pure α-pinene [13], a is the $[\alpha]_D$ of the initial α-pinene, b is the $[\alpha]_D$ of the camphene obtained (in benzene).

The results obtained by investigating two isomerizates, prepared from (V) under different temperature conditions, are given in the table.

Relation Between the Rate Constants of Camphene Racemization Due to the Reversible Interconversion of Camphene ⇌ Tricyclene (k_1) and Due to Carbonium Ion Regrouping (k_2)

No. of isomerizate	Reaction conditions: temperature	Reaction conditions: amount of catalyst (in %)	Reaction conditions: duration (in hours)	$[\alpha]_D$ of the initial α-pinene	Isomerizate compositions: α-pinene (in %)	Isomerizate compositions: camphene + tricyclene (in %)	tricyclene in mixture camphene + tricyclene (in %)	$[\alpha]_D$ of the camphene obtained: calculated	$[\alpha]_D$ of the camphene obtained: found	Δα *	$\frac{k_1}{k_2}$ **
1	160°	0.2	4	+29.6°	50	37.2	10	+69.3°	58.5°	15.6	1 : 1.6
2	100	2	10	+28.3	46	39.5	9.3	+66.2	56.2	15.0	1 : 1.6

*Calculated by Formula (2).

**Calculated by Formula (1).

On the basis of the data given in the table, it may be considered as established that when (I) is heated with titanic acid at 100 and 160° approximately 40% of it racemizes due to the reversible interconversion (I ⇌ IV) and approximately 60% due to the spatial regrouping of carbonium ions (II) and (III).

A quantitative idea may be obtained of the character of the carbonium ion-conversions leading to racemization of (I) in the presence of titanic acid at 160° by comparing the data from this investigation with those of Roberts and Yansey [5]. By using the isotope method, these investigators showed that under these conditions 50-55% of (I) is racemized by Nametkin regrouping. It follows that the main mass of (I) (over 90%) is racemized on boiling with titanic acid, as a result of two regroupings – Nametkin regrouping and the reversible interconversion (I ⇌ IV). This does not exclude the possibility of a third regrouping, for example Meerwein's as a cause of racemization of (I), but its possible extent is very insignificant and lies at the limits of accuracy of the investigation method.

It should be noted that the sharp decrease in the rate of Nametkin regrouping in comparison with the rate of regrouping observed by Roberts and Yansey when the reaction temperature was lowered from 160 to 100°, is not connected with the transfer of the CH_3-group in the carbonium ion (II) (i. e. tricyclene) and was not confirmed by this investigation. We plan to consider the reasons for this discrepancy in the next reports.

EXPERIMENTAL

Preparation of isomerizate. As starting material we used two carefully purified samples of α-pinene, isolated from natural turpentine of Pinus sylvestris.

First sample: n_D^{20} 1.4655, d_4^{20} 0.8582, $[\alpha]_D$ + 29.6°; second sample: n_D^{20} 1.4654, d_4^{20} 0.8585, $[\alpha]_D$ + 28.3°.

As a catalyst we used titanic acid, described in one of the communications from our laboratory under the name of "catalyst No. 1-52" [14]. The isomerization was carried out in the liquid phase with continuous stirring at 160° (isomerizate No. 1) and at 100° (isomerizate No. 2). When the content of (V) in the isomerizates fell to 45-50% the reaction was stopped. The isomerizates obtained contained fenchene and monocyclic terpenes as well as (I), (IV) and (V).

Quantitative determination of the total camphene and tricyclene in the isomerizates. The quantitative determination of the total (I) and (IV) in the isomerizate was carried out by a method based on their conversion to isobornyl formate and its subsequent hydrolysis [15]. As (V) was present in the isomerizate and 10% of it was converted into the ester under the conditions of the analysis, a correction was made in the analysis results. Fenchenes present in the isomerizate were also converted into isofenchyl ester, but as the amount of fenchenes in the isomerizates, prepared from (V) with titanic acid, was very small and according to our data did not exceed 4-6% of the total of all the esterifiable terpenes, we did not consider it necessary to introduce corrections for the presence of fenchenes, i. e. we considered the fenchenes present as a mixture of (I) and (IV).

Quantitative determination of tricyclene. For the quantitative determination of (IV) in a mixture of (I) and (IV), contained in the isomerizates, 200-300 g of isomerizate was distilled in vacuum through a bubble cap column of about 30 theoretical plates. The distillate was divided up into a large number of fractions of arbitrary amounts. Due to the closeness of the boiling points of the components, the insignificant amount of (IV) in the isomerizates and the comparatively large "retention" of the column, (IV) was not isolated in a pure form but as a mixture with (V), (I) and fenchenes in several head fractions. As the amount of fenchenes in the fractions was very small, these fractions were taken as ternary mixtures of (I), (IV) and (V) and fractions containing (I), (V) and fenchenes, as binary mixtures of (I) and (V).

For the quantitative determination of (IV), we first calculated the specific rotation $[\alpha]_D$ of the total (I) and (IV) in each fraction using Bio's equation:

$$[\alpha]'_D \cdot a + [\alpha]''_D \cdot (1 - a) = [\alpha]_D, \qquad (3)$$

where: $[\alpha]_D$ is the specific rotation of the fraction examined, $[\alpha]''_D$ is the specific rotation of the original α-pinene and a is the amount of combined (I) and (IV) in 1 g of the fraction examined.

The percentage of optically active (IV) in the mixture of (I) and (IV) in each fraction was found from the data obtained using the equation:

$$b = 100 - 100 \cdot \frac{[\alpha]'_D}{[\alpha]'''_D}, \qquad (4)$$

where: b is the percentage contained in the mixture of (I) and (IV) in the given fraction, $[\alpha]'''_D$ is the specific rotation of (I) (in pinene). After this we subsequently calculated the content of (IV) in each fraction, the content of (IV) in the isomerizate and the content of (IV) in the mixture of (I) and (IV) contained in the isomerizate.

The results of the distillations are given in the form of curves (Figs. 1 and 2), from which it may be seen that the optical rotation of the mixture of (I) and (IV) rapidly grows from the initial fraction to the final one, but it settles down at a definite point. The latter occurs when (IV) has been distilled off completely. Hence, the value of the optical rotation corresponding to the horizontal part of the curve (Curve 5 in Figs. 1 and 2), was taken as $[\alpha]'''_D$ for calculations of b by Formula (4).

The results of determining (IV) by the physical analytical method described agree with the results obtained by oxidizing the fractions containing (IV) with an 8% alkali solution of $KMnO_4$ at 60°. Thus, for example, 37.4 g of a mixture of fractions 1-5 of the isomerizate, obtained at 100°, containing 8.15 g of (V) according to the physical analytical data, yielded 11.7 g of a mixture of hydrocarbons:

m. p. +42°, n_D^{54} 1.4476, d_4^{54} 0.8524, $[\alpha]_D$ + 16.24° (in benzene, c = 20), MR_D 42.77; calculated for tricyclic terpene 42.48.

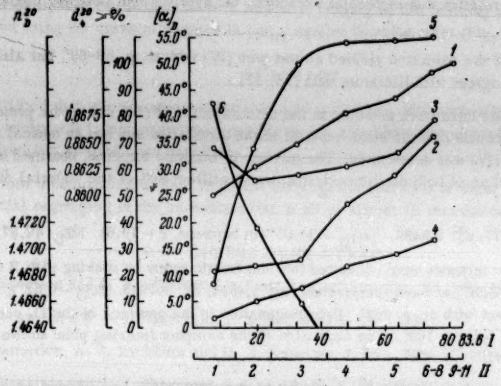


Fig. 1. Distillation of isomerizate No. 1, obtained at 160°. * I) % distilled off, II) number of fraction. 1) $[\alpha]_D$, 2) content of the mixture camphene and tricyclene in percentage, 3) d_4^{20}, 4) n_D^{20}, 5) $[\alpha]_D$ of the mixture of camphene and tricyclene, 6) tricyclene content of the mixture of camphene and tricyclene in percentage.

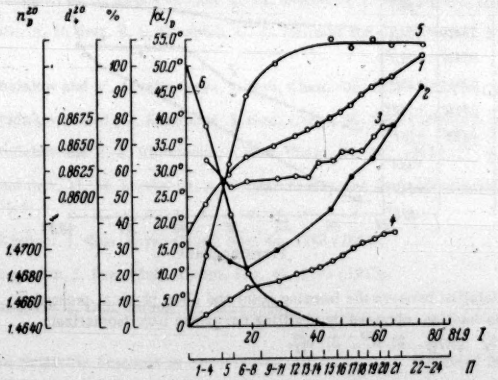


Fig. 2. Distillation of isomerizate No. 2, obtained at 100°. * I) % distilled off, II) number of fraction. 1) $[\alpha]_D$, 2) content of the mixture camphene and tricyclene in percentage, 3) d_4^{20}, 4) n_D^{20}, 5) $[\alpha]_D$ of the mixture of camphene and tricyclene, 6) tricyclene content of the mixture of camphene and tricyclene in percentage.

*Fractions containing monocyclic terpenes are not given.

According to optical rotation and molecular refraction, the hydrocarbons obtained contained 70-80 % of (IV).

Increasing the time of the oxidation yielded almost pure (IV) with m. p. 58-60°, but also led to losses due to partial oxidation, which agrees with literature data [16, 17].

Since high results could have been obtained in the determination of (IV) due to the presence of cyclofenchene, which would concentrate in the head fractions in the distillation and has an optical rotation close to zero, the cyclofenchene in (IV) was determined. The mixture of tricyclic terpenes, obtained after the oxidation described for the head fractions of both the isomerizates, was disstilled; 90% of the material distilled in the range 148-152°:

m. p. 48.5°, n_D^{54} 1.4475, d_4^{54} 0.8496, $[\alpha]_D$ + 14.65° (in benzene, c = 19.6), MR_D 42.87.

The distilled tricyclic terpenes were converted into the formic esters by shaking with 2 moles of 97% HCOOH in the presence of H_2SO_4 at room temperature (n_D^{20} 1.4694, d_4^{20} 1.0058, $[\alpha]_D$ – 0.52°), and the latter were hydrolyzed to isoborneol with m. p. 202°. Dehydrogenation in the presence of $CuCO_3$ converted the latter into camphor with freezing point + 169°. The depression of the camphor freezing point showed that it contained about 5% of isofenchone [18].

From this it follows that the error in determining (IV) by the physical analytical method, due to the presence of cyclofenchene in the isomerizate, did not exceed 5%. Since there was a similar error in the same direction in the determination of the total (I) and (IV), due to the presence of fenchenes, the results of the determination of (IV) were not corrected.

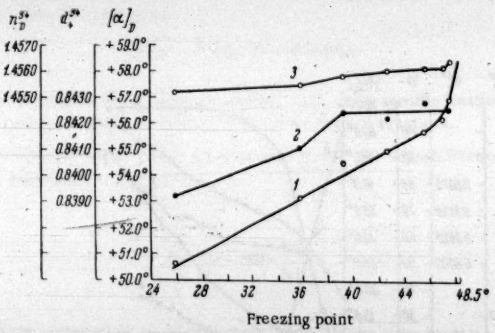


Fig. 3. Relation between the freezing point and other physical properties of separate fractions obtained by distilling camphene from isomerizate No. 1. 1) $[\alpha]_D$, 2) d_4^{54}, 3) n_D^{54}.

Determination of the optical rotation of camphene. The isolation of (I) from both the isomerizates was carried out by a method which we developed especially and which permitted the separation of (I) from a solution in (V) and did not effect its optical activity. The method included a selective oxidation of (V) with $KMnO_4$ in an alkaline medium and a subsequent final purification of (I) by distillation on a high efficiency column in vacuum. Comparison of its physical constants with the physical constants of pure camphene gave us the purity of the (I) isolated:

Freezing point + 48.5°, n_D^{54} 1.4564, d_D^{54} 0.8421 [11].
From the isomerizate obtained at 100°, we isolated (I) with freezing point + 48.5°, n_D^{54} 1.4564, d_4^{54} 0.8425, $[\alpha]_D$ + 56.2° (in benzene, c = 40). From the isomerizate obtained at 160°, we isolated (I) with freezing point + 47.7°, n_D^{54} 1.4564, d_4^{54} 0.8425, $[\alpha]_D$ + 56.9° (in benzene, c = 40).

As the latter camphene contained traces of impurity, judging by the freezing point, the value found for $[\alpha]_D$ was corrected using the curve of changes in $[\alpha]_D$ against freezing point (Fig. 3).

SUMMARY

It was established that when heated with titanic acid at 100 and 160° approximately 40% of the camphene racemized due to reciprocal interconversion of camphene ⇌ tricyclene and about 60% due to spatial regrouping of the carbonium ion formed from camphene.

It is clear from a comparison of data from this investigation and data of other authors that the camphene, racemized by spatial regrouping of the carbonium ion, is all or almost all racemized by Nametkin regrouping.

LITERATURE CITED

[1] S. S. Nametkin and L. Ya. Bryusova, J. Russ. Phys.-Chem. Soc. 60, 265 (1928).

[2] S. S. Nametkin and A. I. Shavrygin, J. Gen. Chem. 4, 847 (1934).

[3] S. S. Nametkin, A. S. Kichkina and D. N. Kursanov, J. Russ. Phys.-Chem. Soc. 61, 1065 (1929).

[4] S. S. Nametkin and A. I. Shavrygin, J. Gen. Chem. 3, 35 (1933).

[5] J. D. Roberts and J. A. Yansey, J. Am. Chem. Soc. 75, 3165 (1953).

[6] S. S. Nametkin and L. G. Bogacheva, J. Russ. Phys.-Chem. Soc. 62, 1335 (1930).

[7] H. Meerwein and K. van Emster, Ber. 53, 1815 (1921).

[8] G. Swann and F. J. Gripwell, Ind. Chemist 24, 573 (1948).

[9] H. Meerwein and F. Montfort, Ann. 435, 207 (1924).

[10] G. A. Rudakov, Z. S. Khomenko and M. M. Shestaeva, J. Gen. Chem. 24, 549 (1954) (T. p. 563).*

[11] J. P. Bain, A. H. Best, B. L. Hampton, G. A. Hawkins and L. J. Kitchen, J. Am. Chem. Soc. 72, 3124 (1950).

[12] G. A. Rudakov and M. M. Shestaeva, J. Gen. Chem. 26, 2357 (1956) (T. p. 2635)*

[13] G. A. Rudakov and M. M. Shestaeva, J. Gen. Chem. 26, 2362 (1956) (T. p. 2641)*

[14] G. A. Rudakov and Z. S. Khomenko, J. Gen. Chem. 24, 337 (1954) (T. p. 345).*

[15] G. A. Rudakov, M. M. Shestaeva, A. T. Marchevsky and Z. S. Khomenko, J. Gen. Chem. 24, 1452 (1954) (T. p. 1437).*

[16] N. M. Kizhner, J. Russ. Phys.-Chem. Soc. 44, 1748 (1912).

[17] S. S. Nametkin, J. Russ. Phys.-Chem. Soc. 45, 1423 (1913).

[18] G. A. Rudakov, J. Gen. Chem. 16, 261 (1946).

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*T. p. = C. B. Translation pagination.

SYNTHESIS FROM 2,4-DICHLOROBUTENE-2

SYNTHESES OF THE CYANAMIDE DERIVATIVE AND THE SECONDARY AMINE AND ITS DERIVATIVES

A. L. Klebansky, V. V. Markin and K. K. Chevychalova

We developed a method of synthesizing amines from 2,4-dichlorobutene-2 by its reaction with ammonia in an alcohol solution. This reaction was studied independently by A. T. Babayan and A. A. Grigoryan [1]. A complex mixture of amines with different degrees of alkylation was formed by reacting 2,4-dichlorobutene-2 with ammonia. The secondary amine di-(2-chlorobuten-2)-amine-4 was the most interesting for organic synthesis. To obtain it, we first used the method developed by Graf [2] for preparing diallylamine. This method consists of reacting the chloride with calcium cyanamide in the presence of an equivalent amount of caustic soda in an aqueous-alcohol medium, with subsequent hydrolysis of the cyanamide derivative obtained, with mineral acids (preferably sulfuric).

$$2CH_3-CCl=CH-CH_2Cl \xrightarrow{Na_2NC\equiv N} \underset{(I)}{(CH_3-CCl=CH-CH_2)_2N-C\equiv N} \xrightarrow[H_2SO_4]{H_2O} \underset{(II)}{(CH_3-CCl=CH-CH_2)_2NH}$$

We were the first to obtain and describe the intermediate product of the secondary amine synthesis – di-(2-chlorobuten-2)-cyanamide-4 (I). The secondary amine (II) was condensed with carbon disulfide in the presence of alkali to form the corresponding sodium dithiocarbamate (III) by the reaction:

$$(II) \xrightarrow[NaOH]{CS_2} \underset{(III)}{(CH_3-CCl=CH-CH_2)_2N-\overset{\overset{S}{\|}}{C}-SNa}.$$

EXPERIMENTAL

Synthesis of di-(2-chlorobutene-2)-cyanamide-4 (I). 310 ml of cold water and 75 g of finely crushed ice were put into a 2 liter, round bottomed flask with a mechanical stirrer, a mercury seal and a wide adapter with two necks. With vigorous stirring and cooling, 104 g of freshly powdered technical calcium cyanamide containing 55% of CaNC≡N (115.5% of the theoretical amount) was gradually run in through one of the necks of the adapter. 165 g of a 35% aqueous solution of NaOH was gradually added to the suspension obtained, over an hour while the flask was cooled with running water so that the temperature of the reaction mixture did not rise above 20°. To the solution of sodium cyanamide 155 g of 2,4-dichlorobutene-2 dissolved in 300 ml of ethyl alcohol (95%) was gradually added from a dropping funnel. The temperature was kept at 20°. The mixture was stirred in the cold for a further 1.5 hours and then heated on a boiling water bath for 3.5 hours while 240 ml of alcohol distilled off during the stirring (on the water bath). The mixture in the flask was cooled, the suspension obtained was filtered on a Buchner funnel and the precipitate was washed with alcohol. Two layers were obtained in the filtrate: the lower was oil and the upper was aqueous. The oily layer was separated off and combined

with a benzene extract from the aqueous layer. The benzene layer was dried over freshly baked sodium sulfate. The benzene was distilled off and the cyanamide derivative obtained was distilled several times in vacuum (b. p. 153-154° at 1-2 mm). The reaction product was a viscous, colorless oil, which rapidly turned yellow in air, d_4^{20} 1.1161, n_D^{20} 1.5027. After repeated distillation it solidified in the cold to crystals with m. p. 26°. After repeated recrystallization from a mixture of alcohol and water the m. p. was 27-28°. The yeild was 55-60%.

Found %: Cl 31.93. $C_8H_{12}N_2Cl_2$. Calculated %: Cl 32.37.

Synthesis of di-(2-chlorobutene-2)-amine-4 (II). 120 g of di-(chlorobutenyl)-cyanamide and 88 g of sulfuric acid (d 1.84), diluted with 258 ml of water, was placed into a round bottomed 1 liter flask, fitted with a stirrer with a mercury seal and a reflux condenser and heated with an electric heater. It was heated to boiling and stirred for 6 hours. As it boiled the mixture became homogeneous. The solution was cooled, filtered and then decomposed with 130 g of NaOH in 240 ml of water. The amine formed was separated and the remainder was extracted from the alkaline solution with benzene. The benzene solution was dried over solid NaOH. The amine remaining after distilling off the benzene was distilled several times in vacuum:

b. p. 142-144° at 50 mm, 104-105° at 1 mm; d_4^{20} 1.1017, n_D^{20} 1.4977, MR_D 51.36; Calc. 51.69.*

Found %: Cl 35.75. $C_8H_{13}NCl_2$. Calculated %: Cl 36.57.

Titration of the amine with 0.15 N HCl in the presence of Congo red also confirmed its structure.

The method of synthesizing the amine II may be simplified considerably by hydrolyzing the cyanamide derivative without preliminary purification. Impurities in the latter separate out after the sulfuric acid hydrolysis as an oily residue which may be removed in a separating funnel. The solution of the amine sulfate is washed with benzene. Further treatment and isolation of the pure amine is carried out as in the previous experiment. This method gives about the same yield of secondary amine.

Synthesis of di-(2-chlorobutene-2)-dithiocarbamates (III). 40 g of dichlorobutenylamine was placed in a flask with a dropping funnel and a stirrer and cooled with ice water, and 16 g of carbon disulfide (approximately theoretical amount) and 46.6 g of 18% NaOH solution were gradually added. The concentration of the alkali was varied from 4-18% in our experiments. As the NaOH solution was added, a thick, viscous, yellow mass was initially formed and this gradually liquefied and turned into a golden-yellow solution, which gradually changed to a reddish orange color. The yield of sodium dithiocarbamate was determined by iodometric titration. 0.9485 grams of sodium dithiocarbamate solution used up 8.7 ml of 0.1 N iodine solution, which corresponded to an 87% yield of sodium dithiocarbamate on the amine taken.

Ammonium dithiocarbamate was prepared by an analogous method. Eight grams of CS_2 and 26 ml of an 8% ammonia solution, which corresponded to 2.08 g of NH_3 (theoretically 1.75 g of NH_3 was required), was gradually added to 20 g of amine. A clear, wine-red solution was obtained. Titration with methyl red as the indicator showed that there was 0.3 g of unreacted NH_3 in the solution or that 1.78 g of NH_3 had combined to form ammonium dithiocarbamate. The dithiocarbamate content of the solution was determined by titration with 0.1 N iodine in KI. The yield of dithiocarbamate was 81%. It is possible that the ammonium dithiocarbamate had partly decomposed.

SUMMARY

1) The reaction of 2,4-dichlorobutene-2 with calcium cyanamide in the presence of an equivalent amount of NaOH was studied. Di-2-(2-chlorobutene-2)-cyanamide-4 (I) was obtained from this reaction.

2) The hydrolysis of (I) was studied; it was established that the secondary amine – di-(2-chlorobutene-2)-amine-4 (II) was formed.

3) The amine (II) was condensed with carbon disulfide in the presence of alkali or ammonia with the formation of the corresponding sodium or ammonium dithiocarbamates (III).

*These data are quite close to the values for the constants found for the secondary amine prepared directly by treating 2,4-dichlorobutene-2 with an alcoholic solution of ammonia (d_4^{20} 1.102, n_D^{20} 1.4979).

LITERATURE CITED

[1] A. T. Babayan and A. A. Grigoryan, Proc. Acad. Sci. Armenian SSR 6, 143 (1947).

[2] P. Graf, J. Am. Chem. Soc. 46, 1307 (1924); Chem. Zentr. 1925, 1, 1242.

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REACTIONS OF METHYL METHACRYLATE WITH ORGANOMAGNESIUM COMPOUNDS

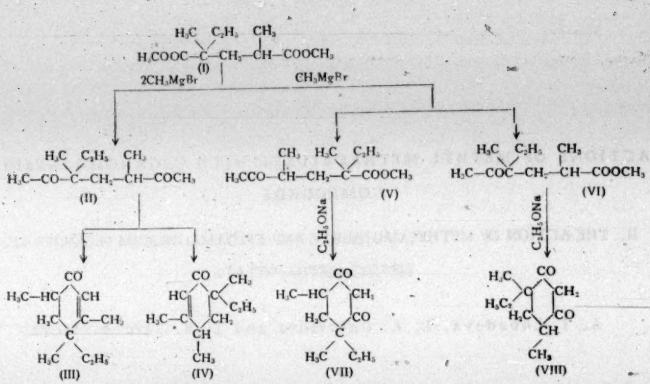
II. THE ACTION OF METHYLMAGNESIUM AND ETHYLMAGNESIUM BROMIDES ON METHYL METHACRYLATE

A. I. Lebedeva, L. A. Gavrilova and T. B. Serdobintseva

Although there have been a whole series of papers on the subject, the mechanism of the formation of terpenes and terpene alcohols from isoprene and dimethylvinylcarbinol is far from clear. In particular, there has been no direct evidence as yet on the part that the alcohol hydroxyl, activated by the catalyst, plays in the dimerization processes. To explain this problem and investigate the process with isoprene homologs and analogs and dimethylvinylcarbinol, we tried to find, first of all, a method for rapid one-stage synthesis of the corresponding ethylenic alcohols. The reaction of isopropyl magnesium bromide with methylmethacrylate [1] and methyl acrylate [2] had been studied previously and dimethyl esters of substituted glutaric acids were found as the main reaction products instead of tertiary ethylenic alcohols. In this work we decided to exclude the possible specific effect of the isopropyl radical and to investigate the reaction of methyl methacrylate with methylmagnesium and ethylmagnesium bromides. Tertiary ethylenic alcohols were obtained in yields of 40 and 25% with methyl and ethylmagnesium bromides, respectively, in contrast to isopropylmagnesium bromide. However, the reaction did not proceed in just one direction, and although it fitted completely within the framework of the system proposed by us earlier for ethylmagnesium bromide [3], it proceeded somewhat differently with methylmagnesium bromide. Dimethyl α, α'-dimethyl-α-ethylglutarate (I) was not detected in the reaction mixture in the latter case. Undoubtedly this ester is formed during the reaction but immediately reacts further with methylmagnesium bromide and either one or both of the methoxyl groups of the ester (I) are substituted by methyl groups (see scheme). When both methoxyl groups are substituted the diketone 3,5-dimethyl-3-ethylheptandione-2,6 (II) is formed which is very readily cyclized to form an unsaturated cyclic ketone of the general formula $C_{11}H_{18}O$ – 3,4,6-trimethyl-4-ethyl cyclohexen-2-one-1 (III) or 2,4,5-trimethyl-2-ethylcyclohexen-5-one-1 (IV). Farghet and Perkin [4] and Harries [5] point out that in the case of heptan-dione-2,6, elimination of water and the formation of 1-methylcyclohexen-1-one-3 proceed quite readily. Harries even considered at one time that heptandione-2,6 was incapable of existing.

Two esters with the general formula $C_{11}H_{20}O_3$ – methyl 1,3-dimethyl-1-ethyl-3-acetobutyrate (V) or methyl 1,3-dimethyl-3-ethyl-3-acetobutyrate (VI) may be formed by the substitution of one methoxyl group of the dimethyl ester (I) by a methyl group. Both these esters give substituted acetobutyric acids on hydrolysis and form the corresponding derivative of dihydroresorcinol, $C_{10}H_{16}O_2$, when treated with sodium ethylate. In the first case, 4,6-dimethyl-4-ethylcyclohexandione-1,3 (VII) may be expected to form, in the second case 4,6-dimethyl-6-ethylcyclohexandione-1,3 (VIII). The dimethylcyclohexandione we obtained titrated as a monobasic acid; the silver salt $C_{10}H_{15}O_2Ag$ was obtained from concentrated solutions of the sodium derivative. All these reactions are analogous to reactions observed with unsubstituted 3-acetobutyric acid. It is known that ethyl 3-acetobutyrate reacts with sodium ethylate to form dihydroresorcinol [6] and titrates with alkalis in the presence of phenolphthalein as a monobasic acid [7].

Thus, the reaction with methylmagnesium bromide proceeds further with the formation of a ketoester and a diketone. By analogy with a whole series of papers [8], when there is an excess of methylmagnesium bromide, together with the substitution of the methoxyl group by a methyl, one would expect the formation of ditertiary glycols.



EXPERIMENTAL

The action of methylmagnesium bromide on methyl methacrylate. The organomagnesium compound was prepared as described in [1] from 13 g of magnesium, 48 g of methyl bromide and 26 g of methyl methacrylate. The synthesis was repeated 4 times. After evaporating off the ether and distilling, two fractions were obtained: the 1st (54.5 g) had b. p. 80-133° and contained ~ 38% of dimethylisopropenylcarbinol and ~ 48% of 3-methylpentanone-2 (determined by oxime formation). The ketone was isolated from the mixture as the semicarbazone with m. p. 94-95°, which corresponded with literature data [9]; the alcohol distilled over the range 118-119° and was characterized by its physical constants. The 2nd fraction (11.8 g) had:

b. p. 103-104° (6 mm), d_4^{20} 0.9770, n_D^{20} 1.4468, MR_D 54.64; Calc. 54.66.

Found %: C 65.72; H 10.09. M 195.5. $C_{11}H_{20}O_3$. Calculated %: C 65.97; H 10.07. M 200.3.

The data correspond to compound (V) or (VI).

A mixture of 18 g of this fraction, 30 g of potash and 150 ml of water was boiled for 5 hours. The neutral products were distilled in steam and extracted from the distillate with ether. After distilling off the ether, 3.0 g of material was obtained:

b. p. 97-98° (10 mm), d_4^{20} 0.9353, n_D^{20} 1.4807; MR_D 50.49. M 166.1. $C_{11}H_{18}O$. Calculated MR_D 50.34. M 166.3.

The semicarbazone had m. p. 192-193° (with decomp.).

Found %: C 64.21; H 9.51; N 18.95. $C_{12}H_{21}ON_3$. Calculated %: C 64.54; H 9.48; N 18.81.

The data corresponded to compound (III) or (IV).

The residue after distillation of the neutral products, was acidified and extracted with ether. After distilling off the ether, we obtained 12.5 g of a syrupy acid, which distilled at 155-160° (6 mm) with slight decomposition.

Found: equiv. 186.5. $C_{10}H_{18}O_3$. Calculated: equiv. 186.3. Found %: C 41.33; H 6.04; Ag 36.98.

$C_{10}H_{17}O_3Ag$. Calculated %: C 40.97; H 5.85; Ag 36.80.

From 1.5 g of the acid and 10 g of hydroxylamine hydrochloride in 110 ml of water, we obtained 1.2 g of an oxime with m. p. 97-103°. After several recrystallizations (from aqueous alcohol), the first fraction of the oxime had m. p. 120-121° and the residue melted at 114-116°.

Found %: N 7.06; equiv. 200.9. $C_{10}H_{19}O_3N$. Calculated %: N 6.96; equiv. 201.3.

A silver salt was prepared from the sodium salt of the acid oxime.

Found %: N 4.56; Ag 34.96. $C_{10}H_{18}O_3NAg$. Calculated %: N 4.57; Ag 35.01.

A mixture of 20 g of ester with b. p. 103-104° (6 mm), 12 g of metallic sodium and 185 ml of alcohol was boiled for 4 hours, diluted with water and a small amount of a neutral product distilled off, which had the same constants as the compound obtained by hydrolysis with potash. After acidification, crystals (11.5 g) separated with m. p. 112-112.5° (from a mixture of acetone and water).

Found %: C 71.67; H 9.58; equiv. 168.2. $C_{10}H_{16}O_2$. Calculated %: C 71.33; H 9.59; equiv. 168.2.

Found %: Ag 39.31. $C_{10}H_{15}O_2Ag$. Calculated %: Ag 39.21.

The data corresponded to compound (VII) or (VIII).

The action of ethylmagnesium bromide on methyl methacrylate. The synthesis was carried out with 13 g of magnesium, 54 g of ethyl bromide and 26 g of methyl methacrylate and was repeated 4 times. After distilling off the ether and distilling the product (89.3 g), two fractions were obtained:

1st (16.4 g) b. p. 150-152°, d_4^{20} 0.8459, n_D^{20} 1.4332, MR_D 39.41; H' 0.97. $C_8H_{16}O'F$. Calculated MR_D 40.20; H' 1.00.

2nd (40.9 g) b. p. 120° (12 mm), d_4^{20} 0.9869, n_D^{20} 1.4395, MR_D 61.45. M 232.0. $C_{12}H_{22}O'_2O''_2$.

Calculated MR_D 60.92. M 230.3.

A mixture of 12 g of this fraction, 6 g of potassium hydroxide and 40 ml of alcohol was boiled for 4 hours. After dilution with water, the alcohol was distilled off. The residue was acidified and extracted with ether. We obtained 6.8 g of an acid with m. p. 65-66° (from water).

Found %: C 59.45; H 8.92; equiv. 100.6. $C_8H_{16}(COOH)_2$. Calculated %: C 59.38; H 8.97; equiv. 101.1.

Found %: Ag 51.83. $C_{10}H_{16}O_4Ag_2$. Calculated %: Ag 51.86.

The acid (6 g) was slowly distilled. At 100-101°, 0.5 g of water distilled off and at 280-281°, 4.6 g of a substance with m. p. 35-36° (from petroleum ether).

Found %: C 65.44; H 8.87. M 175.7. $C_{10}H_{16}O_3$. Calculated %: C 65.19; H 8.75. M 184.2.

SUMMARY

1) It was found that the reaction of methyl and ethylmagnesium bromides with methyl methacrylate proceeded simultaneously in several directions and it was noticed that tertiary ethylenic alcohols: dimethylisopropenylcarbinol (~ 40 %) and diethylisopropenylcarbinol (~ 25 %), were formed in both cases in contrast to isopropylmagnesium bromide.

2) It was established that the reaction with methylmagnesium bromide did not stop with the formation of dimethyl α, α'-dimethyl-α-ethylglutarate (I) but proceeded further with the substitution by methyl groups of one or two methoxyl groups of the complex ester of this acid and in the first case methyl dimethylethyl-3-acetobutyrate (V, VI) was separated as the final reaction product, while in the second, the conversion product of 3,5-dimethyl-3-ethylheptandione-2,6 (II) – trimethylethylcyclohexenone (III or IV) was formed.

3) Dimethylethylcyclohexanedione (VII or VIII) was formed by treating methyl dimethylacetobutyrate with sodium ethylate, and dimethylethyl-3-acetobutyric acid was isolated by hydrolysis.

4) Ethylmagnesium bromide, besides the usual reaction forming diethylisopropenylcarbinol, reacted with methyl methacrylate, similarly to isopropylmagnesium bromide, to form dimethyl α-α'-dimethyl-α-propylglutarate and gave α,α'-dimethyl-α-Propylglutaric acid on hydrolysis; by distillation the latter was converted into the corresponding anhydride.

LITERATURE CITED

[1] A. I. Lebedeva and E. D. Vainrub, J. Gen. Chem. 22, 1974 (1952) (T. p. 2023).*

[2] A. I. Lebedeva and E. D. Vainrub, J. Gen. Chem. 24, 1207 (1954) (T. p. 1195).*

[3] A. I. Lebedeva, Bull. Leningrad State Univ. 1954, 175.

[4] R. G. Fargher and W. H. Perkin, Jr., Chem. Soc. (London) 1914, 1361.

[5] C. Harries, Ber. 47, 784 (1914).

[6] D. Vorländer, Ann. 294, 270 (1897).

[7] R. Schilling and D. Vorländer, Ann. 308, 190 (1899).

[8] M. A. Valeur, Compt. rend. 132, 933 (1901); Z. A. Pogorzhelsky, J. Russ. Chem. Soc. 35, 882 (1903); P. Bruylants, Bull. Acad. Belgique 7, 276 (1909); E. Kislovskaya, J. Russ. Chem. Soc. 45, 1975 (1913); A. D. Petrov and P. S. Sanin, J. Gen. Chem. 8, 195 (1938).

[9] M. A. Courtot, Bull. soc. chim. (3) 35, 982 (1906).

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*T. p. = C. B. Translation pagination.

THE EFFECT OF ULTRASONICS ON AQUEOUS SOLUTIONS OF AROMATIC HYDROCARBONS

M. A. Khenokh and E. M. Lapinskaya

It has been shown in a series of papers that extensive chemical changes occur during the ultrasonic treatment of solutions of various organic compounds [1-6]. It seemed interesting to complete these investigations by studying the effect of ultrasonics on the simplest aromatic hydrocarbons. We considered that besides the intrinsic value of this problem its clarification would shed light on the changes due to ultrasonics in cyclic amino acids, found in protein macromolecules [5].

There is almost no data in the literature on the effect of ultrasonic oscillations (USO) on aromatic hydrocarbons and on the chemical processes occurring there. There is only a reference which states that ultrasonics cause the disappearance of the characteristic absorption spectra in aqueous solutions of benzene and phenol [7].

In the present work saturated aqueous solutions (in 25 ml amounts) of benzene, toluene and phenol solutions were subjected to ultrasonics (435 kc). All the hydrocarbons were chemically pure and freshly distilled preparations. The water was distilled three times. The high-frequency generator and the operating conditions were described earlier [3, 6]. After treatment with ultrasonics for a definite time, samples were taken from the solutions and immediately analyzed on a spectrophotometer SF-4. The measurements were carried out in the region of 230-300 mμ in a vessel with a 5 mm thick layer. Formaldehyde was determined by measuring the optical density of solutions at 520 mμ [8].

The high sensitivity and specificity of this method were confirmed in paper [9]. Phenolic hydroxyls were determined by measuring the maximum at 750 mμ [10] in blue solutions, produced by adding Folin's reagent [11], which is general for phenols.

The standard curve for phenolic hydroxyl content was obtained for phenol solutions of different concentrations.

The effect of ultrasonics on benzene solutions. The results of spectrophotometric examination of ultrasonically treated benzene are given in Fig. 1. An examination of the curves shows that benzene absorption rises in the region of 230-300 mμ with increase in time of ultrasonic treatment. The spectrum of aqueous solutions of benzene changes noticeably even after a short ultrasonic treatment, widening into the short and long wave regions of the spectrum. The intensity of absorption falls in the region of 230-270 mμ after a five minute ultrasonic treatment, but after a longer period of treatment it increases sharply, so that after an hour of treatment the characteristic benzene absorption maximum cannot be detected in the general background of ultraviolet-light absorption. On the basis of absorption changes in aqueous benzene solutions, it is reasonable to suppose that at the beginning of the ultrasonic treatment, splitting of benzene molecules proceeds at the greatest rate. There is an increase in the formation of benzene oxidation products with an increase in time of ultrasonic treatment and due to this, the total absorption rises. The benzene solution became brown under the effect of ultrasonics and the color intensified with time of ultrasonic treatment. The oxidation processes that occur in aqueous solutions [7, 12] during ultrasonic treatment, cause extensive changes in the benzene nucleus. The C–C bond in benzene is destroyed and formaldehyde is formed during treatment with USO. Fig. 2 shows that the amount of formaldehyde increases with increase in the time of ultrasonic treatment and benzene concentration. The formaldehyde yield was 1.05, 1.60, 0.81 amd 1.56% of the original benzene for concentrations of $2.5 \cdot 10^{-3}$ and $10.2 \cdot 10^{-3}$ m after 1 and 3 hour ultrasonic treatments.

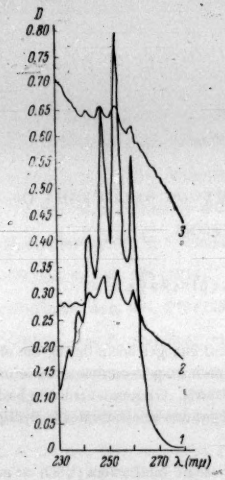

Fig. 1. Absorption curves of benzene solutions. 1) Not treated with ultrasonics; 2) treated with ultrasonics for 5 minutes; 3) treated with ultrasonics for 15 minutes.

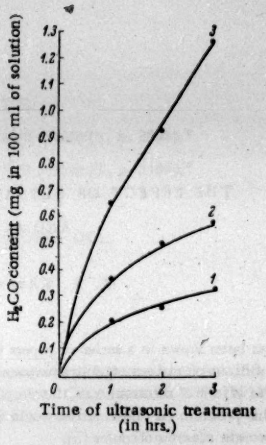

Fig. 2. Ultrasonic effect on formaldehyde formation in benzene solutions of different concentrations. 1) $2.5 \cdot 10^{-3}$ m, 2) $5.0 \cdot 10^{-3}$ m, 3) $10.2 \cdot 10^{-3}$ m.

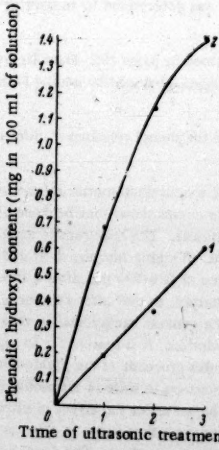

Fig. 3. The effect of ultrasonics on phenolic hydroxyl formation in benzene solutions of different concentrations. 1) $5 \cdot 10^{-3}$ m, 2) $10.2 \cdot 10^{-3}$ m.

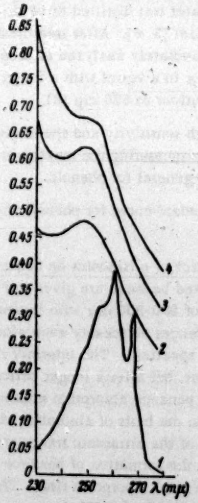

Fig. 4. Absorption curves of toluene solutions. 1) Not treated with ultrasonics; 2) treated with ultrasonics for 15 minutes; 3) treated with ultrasonics for 30 minutes; 4) treated with ultrasonics for 60 minutes.

Ultrasonics cause not only the splitting of the benzene nucleus but also the formation of phenols as a result of free-radical formation during ultrasonic treatment of water [7, 13]. Data on the determination of phenolic hydroxyls in benzene treated with ultrasonics are given in Fig. 3. The results obtained show that the oxidation processes that occur cause the introduction of an OH-group into the benzene nucleus. It can be seen from the curves in Fig. 3 that OH-group formation in a benzene solution increases with increase in time of ultrasonic treatment.

A saturated solution of benzene in water first treated with ultrasonics for 15 hours was prepared to find out what effect the oxidation products, H_2O_2, HNO_2 and HNO_3, which are always formed in aqueous solutions by ultrasonics [7, 12] would have on the changes in benzene. Formaldehyde and phenolic hydroxyls were determined in the benzene solution after keeping for five hours in a thermostat at 40°. Analysis of a benzene solution prepared with water treated by ultrasonics and kept under conditions analogous to those under which ultrasonic treatment was given, showed that it did not undergo noticeable chemical changes. Only traces of formaldehyde and phenols were detected in such a benzene solution.

It may be concluded from the data obtained that chemical changes due to ultrasonic treatment of saturated aqueous benzene solutions are mainly caused not by H_2O_2, HNO_2 and HNO_3, but by the decomposition of water by cavitation into free radicals ($H_2O \rightarrow H + OH$), which cause benzene oxidation.

Effect of ultrasonics on toluene solutions. The ultraviolet absorption curves of toluene solutions are shown in Fig. 4, from which can be seen that there is an increase in the general absorption of toluene solutions under ultrasonic treatment; the absorption maxima, characteristic for toluene, disappear on the curves after only a 15 minute ultrasonic treatment. Simultaneously with an increase in absorption density, the ultrasonic oscillations induce changes in toluene which are accompanied by the formation of a new maximum at 250-251 mμ. It may be concluded from the spectrum analysis that USO cause extensive chemical reactions in toluene solutions. Specifically, the data on formaldehyde determination (table) indicate that under the effect of ultrasonics, toluene undergoes destructive oxidation with the breaking of carbon-carbon bonds. The formaldehyde yields after 1, 2 and 3 hours ultrasonic treatments are 1.08, 1.28 and 1.53% of the original toluene, respectively.

The Effect of Ultrasonics on the Formation of Formaldehyde and Phenolic Hydroxyls in Toluene Solutions

Time of ultrasonic treatment (in hours)	Formaldehyde (in mg per 100 ml of solution)	OH-groups (in mg per 100 ml of solution)
1	0.51	0.27
2	0.60	0.54
3	0.72	0.58

The formation of phenols then indicates that besides undergoing decomposition processes, toluene is converted into a new compound, retaining a six-membered ring.

The effect of ultrasonics on phenol solutions (0.01 M). In connection with the above data, it seemed interesting to find out the effect of ultrasonic treatment of phenol. The results of spectrum analysis of phenol solutions are given in Fig. 5. It can be seen from the curves that even a prolonged ultrasonic treatment has no noticeable effect on the absorption spectrum of phenol. As the time of ultrasonic treatment is increased there is only an insignificant increase in absorption density of phenol solutions; while the absorption maxima remain at 270 and 276 mμ. By comparison of the effect of ultrasonics on changes in the spectra of benzene, toluene and phenol solutions, the latter turned out to be the most stable. Apparently, the stability of absorption spectra to ultrasonic treatment in aromatic compounds depends to a considerable degree on the character of the substituent in the six-membered ring.

In phenol solutions as in benzene and toluene solutions, the six-membered ring is decomposed by ultrasonics with the formation of formaldehyde.

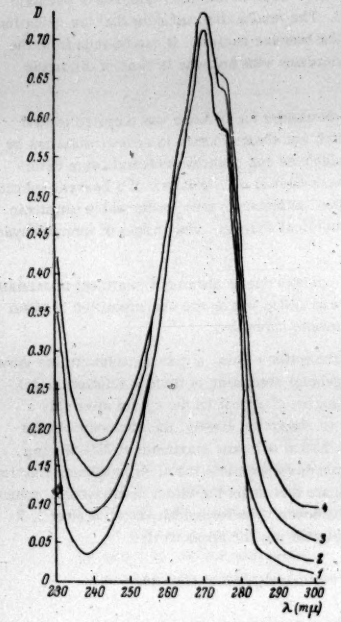

Fig. 5. Absorption curves of phenol solutions. 1) Not treated with ultrasonics; 2) treated with ultrasonics for 1 hour; 3) treated with ultrasonics for 2 hours; 4) treated with ultrasonics for 3 hours.

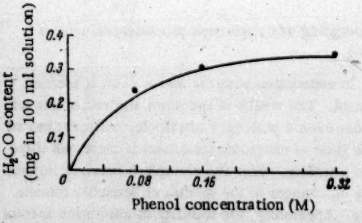

Fig. 6. Effect of ultrasonics on formaldehyde formation in phenol solutions of different concentrations (2 hour ultrasonic treatment).

The data, given in Fig. 6, show that the formaldehyde yield increases with increase in concentration of the phenol solutions. However, it can be seen from the curve in Fig. 6 that the sharpest increase in formaldehyde formation under the effect of ultrasonics occurs in dilute phenol solutions. The formation of formaldehyde is retarded and its yield is decreased by an increase in the phenol concentrations. Thus, after a 2 hour ultrasonic treatment of a 0.08 M phenol solution 0.03% of formaldehyde was formed and for a 0.32 M solution, 0.01% on the weight of phenol.

SUMMARY

1) It was shown that ultrasonic oscillations cause a sharp change in the absorption spectra in the region of 230-300 mμ in solutions of benzene and toluene. A short ultrasonic treatment causes a fall in absorption density in benzene solutions. With a more prolonged ultrasonic treatment the ultraviolet absorption increases and the benzene spectrum disappears. Due to the effect of ultrasonics the optical density increases in toluene solutions; the characteristic toluene absorption maxima disappear on the curves of ultraviolet absorption, and new absorption bands appear with λ_{max} at 250-251 mμ.

2) The absorption spectrum of phenol solutions changes little in relation to the duration of ultrasonic treatment; the ultraviolet light absorption increases only very slightly and retains the absorption maxima of the original phenol.

3) It was shown that the oxidative processes, arising from the ultrasonic oscillations, cause the destruction of the six-membered ring with formation of formaldehyde. Reactions leading to phenol formation occur simultaneously with this, in benzene and toluene solutions.

LITERATURE CITED

[1] I. I. Zhukov and M. A. Khenokh, Proc. Acad. Sci. USSR 68, 333 (1949).

[2] M. A. Khenokh, Report on the Scientific Works of Members of the High-Molecular Weight Compounds, D. I. Mendeleev All-Union Chem. Soc. 2, 32 (1951).

[3] M. A. Khenokh and E. M. Lapinskaya, Proc. Acad. Sci. USSR 80, 921 (1951).

[4] E. M. Lapinskaya and M. A. Khenokh, J. Gen. Chem. 23, 1464 (1953) (T. p. 1531).*

[5] E. M. Lapinskaya, A. H. Mironova and M. A. Khenokh, Proc. Acad. Sci. USSR 94, 109 (1954).

*T. p. = C. B. Translation pagination.

[6] M. A. Khenokh, Proc. Acad. Sci. USSR 97, 871 (1954); J. Gen. Chem. 25, 928 (1955) (T. p. 893).*

[7] L. Bergmann, Der Ultraschall (1954).

[8] M. Tannenbaum and C. E. Bricker, Anal. Chem. 23, 354 (1951).

[9] Yu. Yu. Lurye and Z. V. Nikolaeva, Factory Lab. 20, 674 (1954).

[10] G. R. Freeman, A. B. Van Cleave and J. W. T. Spinks, Can. J. Chem. 31, 448 (1953).

[11] F. D. Snell and C. T. Snell, Colorimetric Methods of Analysis (1953), III, 116.

[12] I. G. Polotsky, J. Gen. Chem. 17, 649, 1048 (1947); J. Phys. Chem. (USSR) 22, 787 (1948).

[13] A. Henglein, Makromol. Chem. 14, No. 1, 15 (1954).

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*T. p. = C. B. Translation pagination.

INVESTIGATION OF THE REACTIONS OF ACETALDEHYDE ON SOME SOLID CATALYSTS

I. CONVERSION OF ACETALDEHYDE AND MIXTURES OF IT WITH WATER ON S. V. LEBEDEV'S CATALYST

Yu. A. Gorin and G. A. Sergicheva

Conversions of acetaldehyde on several solid catalysts at high temperatures give rise to condensation products which include: crotonaldehyde, hexadienal and octatrienal [1-4]. Materials of various degrees of complexity [6, 7] are formed by acetaldehyde at high temperatures (200-450°) on S. V. Lebedev's catalyst [5], which is used for obtaining divinyl from ethyl alcohol and consists of two components with dehydrogenating and dehydrating functions. Besides crotonaldehyde, acetone was found in this reaction as well as more complex products which separated as an oil. Furthermore, CO, CH_4, CO_2, propylene, butylene and divinyl were detected in the gas. I. A. Livshits [8] and then Yu. A. Gorin and I. K. Gorn [9] investigated the composition of the oil containing the more complex products of aldehyde condensation, and found benzaldehyde in it. However, these materials were not studied in greater detail although such an examination could elucidate the formation of some side products of S. V. Lebedev's reaction, most of which, as was shown earlier by one of us, are obtained through acetaldehyde.

We investigated the conversion of acetaldehyde on S. V. Lebedev's catalyst as well as on its components (dehydrogenating and dehydrating), as we were mainly interested in studying the composition of the liquid reaction products. We also investigated the effect of diluting the aldehyde with water on its conversion on these catalysts.

We were able to separate only a part of the relatively simple materials from the mixture of different conversion products thus obtained. The more complex compounds remained unstudied due to the difficulty of identifying them. In agreement with the data in the papers cited above CO, CH_4, H_2, CO_2, C_2H_4, divinyl and unsaturated C_3 and C_4 hydrocarbons, which were a mixture of propylene and butylene, were detected in the gas. Acetone, crotonaldehyde and benzaldehyde were found in the liquid products. Besides these materials which had been detected earlier in acetaldehyde condensation products [7, 8, 9], o-tolualdehyde and o-xylene were also found. Furthermore, on investigating the liquid products obtained in experiments on dehydrogenating and dehydrating components, evidence was found that sorbic aldehyde was also present.

The results of experiments with the aldehyde and its aqueous mixtures are given in Table 1. On dilution of the aldehyde with water, the products of cracking (CO and CH_4) decrease and the amount of the binary condensation products of acetaldehyde—crotonaldehyde increases. Oil formation (higher condensation products) also decreases.

The reactions giving rise to the materials detected in products of acetaldehyde conversion on S. V. Lebedev's catalyst seemed very interesting. As S. V. Lebedev supposed [5], CO and CH_4 are, without doubt, obtained by the decomposition of acetaldehyde.

However, as the data in Table 1 show, the amount of methane in the gas is greater than that of carbon monoxide in experiments on the catalyst and its dehydrogenating component, while at the same time the reverse

happens in experiments on the dehydrating component. Apparently, besides reaction (I), there are other sources of methane and carbon monoxide formation (see below). In particular, the formation of excess carbon monoxide in experiments on the dehydrating component may be explained by the decomposition of higher aldehydes (acetaldehyde condensation products) by a reaction, analogous to (I).

TABLE 1

Conversion of Acetaldehyde and Mixtures of it with Water on S. V. Lebedev's Catalyst and its Dehydrogenating and Dehydrating Components.*

Test No.	Ratio aldehyde : water (M)	Mixture passed through furnace (in g)	Gas obtained (l) (NTP)	Gas comp. (vol. %)							Extent of aldehyde con. (in %)	Yield of basic reaction products, on reacted acetaldehyde (wt. %)				
				CO_2	C_2H_4	$C_2H_6 + C_3H_8$	C_4H_{10}	CO	H_2	CH_4		crotonaldehyde	higher condensation product (oil)	acetone	divinyl	methane
S. V. Lebedev's catalyst																
1	1 : 0	44	4.3	47.0	2.4	9.0	10.4	6.3	10.2	14.8	92.5	5.5	28.7	1.0	2.7	1.1
2	1 : 2	80	3.95	49.7	2.3	9.8	14.2	2.7	12.1	9.1	82.7	9.5	17.5	4.3	3.7	0.7
3	1 : 4	116	3.65	49.3	3.0	11.9	14.1	2.8	13.0	5.8	72.8	12.1	11.5	4.9	3.9	0.4
Dehydrogenating component																
4	1 : 0	44	3.6	37.9	1.9	6.1	1.9	16.1	11.6	25.1	80.7	10.0	28.2	1.8	0.5	1.8
5	1 : 8	188	3.3	56.3	1.2	5.3	0.6	2.1	21.6	12.6	61.6	16.9	17.8	5.3	0.2	1.1
Dehydrating component																
6	1 : 0	44	1.9	22.7	13.2	14.5	1.9	24.8	5.1	17.8	68.1	10.4	18.9	0.9	0.3	0.8
7	1 : 4	116	1.0	16.7	23.6	16.6	1.4	23.1	2.8	16.1	47.0	16.9	11.6	—	0.2	0.5
8	1 : 8	188	0.8	15.2	25.0	17.5	1.2	26.2	3.1	12.2	39.3	26.5	8.1	0.0	0.15	0.4

*The average data from two experiments are given.

An increase in the amount of CO_2, H_2 and acetone was noticed in experiments carried out on the dehydrogenating component with water-diluted aldehyde. These phenomena are explained well by reactions (II, III and IV) [10, 11], whose relative proportions, apparently, increase when water is added to the aldehyde.

$$CH_3{-}CHO \rightarrow CO + CH_4 \qquad (I)$$

$$\left.\begin{array}{c} 2CH_3CHO \rightarrow C_2H_5COOCH_3 \xrightarrow{H_2O} CH_3COOH + C_2H_5OH \\ \text{or} \\ 2CH_3CHO + H_2O \rightarrow CH_3COOH + C_2H_5OH \end{array}\right\} \qquad (II)$$

$$2CH_3COOH \rightarrow CH_3COCH_3 + CO_2 + H_2O \qquad (III)$$

$$C_2H_5OH \rightarrow H_2 + CH_3CHO \qquad (IV)$$

Crotonaldehyde is formed from acetaldehyde through aldol by reaction (V):

$$2CH_3{-}CHO \rightarrow H_2O + CH_3{-}CH{=}CH{-}CHO. \qquad (V)$$

The formation of a small amount of divinyl in aldehyde decomposition experiments on S. V. Lebedev's catalyst may be explained by the reaction, proposed earlier by one of us [7]:

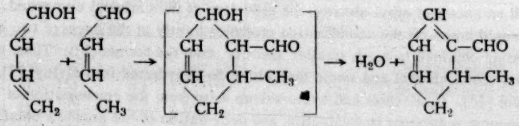
$$CH_3{-}CH{=}CH{-}CHO + 2H \rightarrow CH_3{-}CH{=}CH{-}CH_2OH, \qquad (VI)$$

$$CH_3{-}CH{=}CH{-}CH_2OH \rightarrow H_2O + CH_2{=}CH{-}CH{=}CH_2. \qquad (VII)$$

It is possible that the hydrogen donor necessary for crotonaldehyde reduction is either ethyl alcohol, formed by reaction (IV), or aldol, obtained as an instable intermediate in reaction (V), due to its secondary alcohol group.

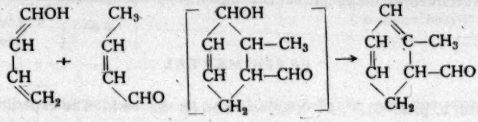
Under the conditions of the S. V. Lebedev reaction, crotonaldehyde undergoes further conversion. It can be seen from Table 1 that in all cases the addition of water to the aldehyde increases the relative amount of crotonaldehyde formation and lowers the yield of higher condensation products. Thus, it may be concluded that the formation of condensation products proceeds through crotonaldehyde. Sorbic aldehyde $CH_3-CH=CH-CH=CH-CHO$ (VIII) may be formed by the reaction of crotonaldehyde and acetaldehyde on the components of S. V. Lebedev's catalyst.

Materials with an open chain may be formed by the reaction of two crotonaldehyde molecules; however, it is extremely probable that these products would be cyclized by the effect of high temperature with the formation of more stable forms [12]. It may be supposed that crotonaldehyde undergoes condensation to give o-dihydrotolualdehyde in a way similar to that considered by Bernhauer and Irrgang [13]. We also suppose that cyclization is likewise possible as a result of the reaction of two crotonaldehyde molecules by the diene synthesis reaction, and one of the molecules probably reacts in the enol form [14].



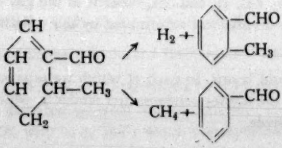
(IX)

or in the other configuration



(X)

o-Dihydrotolualdehyde, which is formed by the reactions (IX) or (X), is an intermediate product from which o-tolualdehyde and benzaldehyde are obtained by reactions (XI) and (XII)

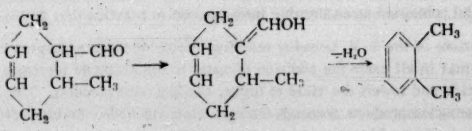


(XI)

(XII)

We proved the existence of reaction (XII) by passing o-dihydrotolualdehyde over S. V. Lebedev's catalyst at 400°. Methane (up to 60% in the gas) and benzaldehyde were found in the decomposition products. This reaction probably explains the high methane content, relative to the carbon monoxide content, in the gas from experiments with acetaldehyde on S. V. Lebedev's catalyst and on its dehydrogenating component.

The formation of aromatic hydrocarbons (o-xylene) from acetaldehyde under conditions of heterogeneous catalysis seemed a very interesting reaction. We did not find any descriptions in the literature of such acetaldehyde conversions on solid catalysts. o-Xylene formation may be explained by the conversion of divinyl (obtained in our experiments) on S. V. Lebedev's catalyst. Ya. M. Slobodin [15] had proposed a similar explanation for the formation of o-xylene as a side product in the preparation of divinyl from alcohol [5]. On the other hand, o-xylene formation may be explained in our reactions by the reaction of divinyl with crotonaldehyde and subsequent conversion of the product obtained by the type of reaction observed by A. A. Petrov and N. P. Sopov [16]. To us this seems a possible hypothesis.



The question arises: why is there in the S. V. Lebedev process such a small amount of cyclic and aromatic materials that could be obtained from acetaldehyde, formed by ethyl alcohol dehydrogenation, while the main mass of the products are compounds with an open chain (C_4 and C_6)? This is explained by the fact that under the conditions of S. V. Lebedev's reaction, acetaldehyde cannot undergo extensive condensation as, on the one hand, it is limited by its small concentration relative to ethyl alcohol, and on the other, by the reduction of acetaldehyde condensation products with ethyl alcohol into the corresponding alcohols [10], which do not undergo further condensation.

Apparently, with an excess of ethyl alcohol, the reduction of the carbonyl compound, arising from acetaldehyde condensation would break off the condensation processes mostly at the stages of two and three unit condensation (the latter being obtained in much smaller quantity than the former [5]). Thus, the crotonaldehyde would be converted into crotyl alcohol and would then either be dehydrated into divinyl [7], or regrouped and reduced to butyl alcohol [10]. C_6 alcohols and hydrocarbons arise from the condensation of crotonaldehyde with acetaldehyde and subsequent reduction, isomerization and dehydration of the products obtained [10].

Aromatic compounds [5], although in very insignificant amounts, are, nevertheless, also obtained as side products in the S. V. Lebedev process. It seems likely on the basis of the results of this work that their formation may also proceed by acetaldehyde condensation, accompanied by the cyclization and aromatization of the condensation products.

EXPERIMENTAL

Acetaldehyde with b. p. 21-21.5°, d^{15} 0.788 was used for the work. The experiments were carried out in a laboratory electric furnace described earlier [17]. 150 ml of catalyst was loaded into the quartz reaction tube. The aldehyde alone, or mixed with water, was fed into the furnace through a cooled connection at a rate of 1 ml per min. The experiments were carried out at 400°. After each experiment the catalyst was regenerated with air at 500°. The gaseous and liquid products were collected by the method described previously [7].

The CO_2, $C_3H_6 + C_4H_8$, C_2H_4, O_2, CO, H_2 and CH_4 content of the gas was determined by absorption in an Orsat apparatus and combustion. The divinyl was determined by the weight of the tetrabromide obtained on brominating the gas.

The condensate formed two liquid layers, in each of which we separately determined: acetaldehyde, crotonaldehyde [7], acetone [18] and the higher condensation products which were contained in the upper layer [7] and boiled higher than crotonaldehyde.

1. Catalytic conversion of acetaldehyde on S. V. Lebedev's catalyst. The results of the experiments with acetaldehyde alone and mixed with water are given in Table 1. (Experiments 1, 2 and 3). To accumulate and investigate the liquid products, 2860 g of acetaldehyde (in portions of 100 ml) was passed through the furnace; 250 liters of gas was isolated. We obtained 2261 g of two-layered condensate (53% by weight in the upper, 47% in the lower).

By salting out and distilling, we obtained from the lower aqueous layer a considerable amount of a fraction with b. p. 102-104°, which was crotonaldehyde, n_D^{20} 1.4359; m. p. of 2,4-dinitrophenylhydrazone, 188-189° [19, 20]; oxidation yielded crotonic acid with m. p. 70° [19]. The upper layer (1188.2 g) was distilled in a stream of nitrogen to separate acetaldehyde and crotonaldehyde from the more complex condensation products. The residue was a dark, viscous liquid. An attempt to separate higher aldehydes from it by treatment with sodium bisulfite solution did not give positive results. For this reason the residue was distilled without a preliminary separation of the aldehydes. In the distillation of the complex mixture of materials, contained in the residue,

their boiling points changed and this made the separation and identification of the reaction products difficult. The residue was distilled on a column at 2-4 mm. Traps cooled to −70° were used to collect the volatile materials under vacuum. A series of fractions was obtained, boiling over intervals of 4-5°, which were distilled in an atmosphere of nitrogen (to determine their boiling range at normal pressure). The aldehyde content of the fractions obtained was determined with hydroxylamine hydrochloride. 2,4-Dinitrophenylhydrazones were prepared and their melting points determined. The aldehydes, contained in the fractions, were oxidized with moist silver oxide to yield acids, which were extracted with ether after decomposition of the salts, recrystallized from hot water and their melting points determined. The results of distilling 521.7 g of material are given in Table 2.

TABLE 2

Results of Examining the Fractions Obtained by Distillation of the Residue Containing the Higher Condensation Products of Acetaldehyde

Fraction No.	Boiling point	Amount (in weight %)	Melting point			Aldehyde corresponding to the derivatives obtained	Content of the aldehyde (in % of the weight of the fraction)
			2,4-dinitrophenylhydrazone	phenylhydrazone	acid from oxidation of aldehyde		
1	115—145°	3.3	188° [19]	—	—	Crotonaldehyde	11.5
2	145—155	3.1	235 [21]	—	121° [22]	Benzaldehyde	—
3	155—160	2.8	235	—	121.5	"	19.0
4	160—170	4.8	235	155° [19]	121.5	"	42.0
5	170—175	5.6	234	—	121.5	"	47.3
6	175—180	5.5	194	—	119	Benzaldehyde +	54.0
7	183—185	3.5	193	—	—	+ o-tolualdehyde	42.9
8	189—194	3.4	193.5 [21]	106 [21]	—	o-tolualdehyde	47.0
9	Residue + losses	68.4				o-tolualdehyde	

Elementary composition of the acid with m. p. 121.5°, obtained from oxidation of the fraction 170-175°. Found %: C 68.71, 68.61; H 5.17, 5.10. C_6H_5COOH. Calculated %: C 68.85; H 4.91.

A mixed m. p. with benzoic acid was not depressed. The molecular weight in dioxane and the nitrogen content (microanalysis) were determined for the 2,4-dinitrophenylhydrazone with m. p. 193-193.5° [21], obtained from fraction 189-194°.

Found %: N 18.27, 19.07. N 288.9. $C_{14}H_{12}O_4N_4$. Calculated %: N 18.66. M 300.

Thus fraction 170-175° contained benzaldehyde, and fraction 189-194°, o-tolualdehyde.

Part of the higher condensation products of acetaldehyde (170 g) was heated over metallic sodium for 48 hours. Hydrocarbons (110 g) were distilled off from the tar obtained, on a column (45 theoretical plates): this gave a fraction equal to about 10% with b. p. 143°, which corresponded to the b. p. of o-xylene, d_4^{20} 0.8805, n_D^{20} 1.5036.

Found %: C 90.07, 90.31; H 10.02, 9.52. M 104.2, 104.6; MR_D 35.15. $C_6H_4(CH_3)_2$. Calculated %: C 90.56; H 9.94; M 106; MR_D 35.55.

Literature data [23] for o-xylene: b. p. 143.9-144.2°, d_4^{20} 0.8812, n_D^{20} 1.5050.

2.0 g of the fraction was oxidized with dilute nitric acid. After recrystallization from hot water, the oxidation product melted at 102-104°, which corresponds to the melting point of o-toluic acid (102°; 105° [22]).

The combination light-scattering spectrum (in cm^{-1}) of the fraction examined was determined with visual estimation of the intensities:

179(3.5), 257(3), 503(3), 579(5), 676(0.5), 733(12), 980(2), 1047(8), 1119(0.3), 1154(3), 1223(7), 1317(0.5*), 1384(4), 1450(2.5), 1577(3), 1600(11).

*Broad.

Literature data for the spectrum of o-xylene [24]: 179(6), 256(5), 506(5), 582(7), 733(10), 986(4), 1051(7), 1118(0), 1158(2), 1222(7), 1287(4), 1384(4), 1450(4), 1584(1), 1606(5).

From comparison of the frequencies of the spectrum we obtained with the frequencies of the o-xylene spectrum, it is obvious that they agree with each other very well. Thus the data found confirm the presence of o-xylene in the hydrocarbons.

2. Catalytic conversion of acetaldehyde on the dehydrogenating component of S. V. Lebedev's catalyst. The results of experiments with acetaldehyde alone and mixed with water on the dehydrogenating component are given in Table 1 (Experiment 4, 5).

A series of experiments were carried out to obtain a sufficient amount of condensate for its more detailed investigation. 344 g of acetaldehyde was put through the furnace (in portions of 50 ml) and 256 g of a two-layered condensate was obtained. The reaction products were investigated exactly as described above. The higher condensation products were distilled. An initial fraction distilled off up to 120° and the crotonaldehyde came over at this point: 2,4-dinitrophenylhydrazone m. p. 184°. The distillation residue (63 g) was distilled in vacuum. Part of the fractions obtained by this distillation were distilled in a stream of nitrogen to determine the boiling point at atmospheric pressure. From the fractions with b. p. 145-150° and 150-176°, (6.8%) we prepared a 2,4-dinitrophenylhydrazone with m. p. 235° and a phenylhydrazone with m. p. 158°, which proved the presence of benzaldehyde. Its content in these fractions was about 50%. From a fraction with b. p. 46-63° (14 mm, 11.5%), we prepared a phenylhydrazone with m. p. 99-103° [19], which corresponded to sorbic aldehyde.

3. Catalytic conversion of acetaldehyde on the dehydrating component of S. V. Lebedev's catalyst. The results of experiments with acetaldehyde alone and mixed with water are given in Table 1 (Experiment 6, 7 and 8) for the dehydrating component. The condensates from all the experiments were combined. The lower, aqueous layer contained unreacted acetaldehyde and crotonaldehyde, which were extracted with ether, and after distilling the acetaldehyde and ether off from the extract, a fraction was isolated with b. p. 102-104°, from which we prepared a 2,4-dinitrophenylhydrazone with m. p. 187-188° (crotonaldehyde). The upper layer of the condensate was distilled in vacuum. From the fraction, whose boiling point corresponded to that of benzaldehyde, we prepared a 2,4-dinitrophenylhydrazone with m. p. 235-236° [21]. From the fraction which was close to the boiling point of sorbic aldehyde, we prepared a semicarbazone with m. p. 205-206°, which corresponded to the semicarbazone of sorbic aldehyde [19].

TABLE 3

Catalytic Decomposition of o-Dihydrotolualdehyde on S. V. Lebedev's Catalyst at 400°

Experiment number	Aldehyde taken (in g)	Gas obtained (in ml)	Condensate obtained (in g)	Composition of the gas (in vol. %)				
				CO_2	olefins	CO	H_2	CH_4
1	11.5	340	8.2	17.5	1.8	9.0	7.6	60.0
2	9.0	160	5.8	21.2	4.2	12.2	8.0	54.0

4. Conversion of o-dihydrotolualdehyde into benzaldehyde on S. V. Lebedev's catalyst. The o-dihydrotolualdehyde used was prepared and characterized as described by Bernhauer [13]. The experiments were carried out in a vertical electric microfurnace, in a quartz reaction tube, which was loaded with 18 ml of catalyst as a layer 12 cm deep. The o-dihydrotolualdehyde was passed through the furnace at a rate of 0.25 ml/min. Then 15 ml of water was passed through to displace the product. The gas was analyzed by the methods described above; after combustion of the hydrogen over copper oxide, the methane was determined by combustion over platinum wire and absorption of the CO_2 in alkali. The results of two experiments are given in Table 3. The condensate was a two-layered liquid.

After separation and drying over $CaCl_2$, the upper layer was finally distilled in vacuum in a stream of nitrogen. A fraction, which was about 20% and had b. p. 54-69° (12 mm) was isolated, and corresponded to benzaldehyde. By oxidizing it with silver oxide, an acid was obtained, which (after recrystallization from hot water) had m. p. 121-121.5° and corresponded to benzoic acid.

Thus we obtained methane and benzaldehyde from the decomposition products of o-dihydrotolualdehyde on S. V. Lebedev's catalyst at 400°. A certain amount of hydrogen, found in the gas, indicated the possibility of dehydrogenation of the o-dihydrotolualdehyde into o-tolualdehyde.

SUMMARY

1) We investigated the composition of acetaldehyde condensation products, obtained at 400° on S. V. Lebedev's catalyst and its dehydrogenating and dehydrating components.

2) Besides crotonaldehyde and benzaldehyde which had been detected earlier, o-tolualdehyde and o-xylene were also present in products obtained on S. V. Lebedev's catalyst. Crotonaldehyde, benzaldehyde and possibly sorbic aldehyde were also found in the products obtained on dehydrogenating and dehydrating components of S. V. Lebedev's catalyst.

3) The dehydrogenating and dehydrating components of S. V. Lebedev's catalyst, while differing in their catalytic effect on alcohol, have the same condensation effect on acetaldehyde and lead to the formation of crotonaldehyde, benzaldehyde and other materials.

4) It was shown that dilution of acetaldehyde with water increases the yield of crotonaldehyde and decreases the yield of higher condensation products.

5) It was shown that o-dihydrotolualdehyde decomposes on S. V. Lebedev's catalyst at 400° to give methane and benzaldehyde.

6) A scheme was proposed which explained the formation of various products from acetaldehyde on S. V. Lebedev's catalyst at high temperature. The formation of aromatic compounds from acetaldehyde passed through the intermediate stage of crotonaldehyde.

LITERATURE CITED

[1] C. Engelder, J. Phys. Chem. 21, 676 (1917).

[2] A. E. Chichibabin, J. Russ. Chem. Soc. 47, 703 (1915).

[3] German Patent No. 349915; C. A. 4, 43 (1927).

[4] P. Sabatier, Compt. rend. 166, 632 (1918).

[5] S. V. Lebedev, J. Gen. Chem. 3, 698 (1933).

[6] S. V. Lebedev, Yu. A. Gorin and S. N. Khutoretskaya, Synthetic Rubber (USSR) 1935, No. 1, 8.

[7] Yu. A. Gorin, J. Gen. Chem. 16, 283, 1089 (1946); Trans. All-Union Sci. Research Inst. Synthetic Rubber 1, 5 (1948).

[8] I. A. Livshits and S. I. Ilina, Trans. All-Union Sci. Research Inst. Synthetic Rubber 1, 42 (1948).

[9] Yu. A. Gorin and I. K. Gorn, J. Gen. Chem. 18, 646 (1948).

[10] Yu. A. Gorin, Trans. All-Union Sci. Research Inst. Synthetic Rubber 3, 17 (1951).

[11] Yu. A. Gorin and N. A. Kalinicheva, J. Gen. Chem. 22, 1256 (1952) (T. p. 1303).*

[12] Yu. A. Gorin and K. N. Charskaya, J. Gen. Chem. 13, 131 (1943).

[13] K. Bernhauer and K. Irrgang, Ann. 525, 43 (1936).

[14] K. Bernhauer and G. Neubauer, Biochem. Z. 251, 173 (1932).

[15] Ya. M. Slobodin, J. Gen. Chem. 5, 1415 (1935).

[16] A. A. Petrov and N. P. Sopov, J. Gen. Chem. 24, 298 (1954) (T. p. 299).*

*T. p. = C. B. Translation pagination.

[17] S. V. Lebedev, Life and Works (United Sci.-Tech. Press, 1938), 515.

[18] V. V. Chelintsev and E. K. Nikitin, J. Gen. Chem. 3, 319 (1933).

[19] Dict. of Organic Compounds 1, 210, 578 (1949); 3, 633, 778 (1949).

[20] Beilst. II Erg. 1, 379 (1928).

[21] J. Wilen, Identification of Pure Organic Compounds (1949).

[22] Beilst. IX, 96, 462 (1926).

[23] Beilst. V, 361-370 (1922); Erg. V, 178-185 (1928).

[24] L.-B.-T. II, 978-981 (1935).

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*T. p. = C. B. Translation pagination.

INVESTIGATION IN THE FIELD OF CONJUGATED SYSTEMS

LXVII. CONDENSATION OF PROPARGYLALDEHYDE WITH 2-HALOGENO- AND 2-ALKOXYBUTADIENES

A. A. Petrov and N. P. Sopov

Propargylaldehyde readily undergoes a diene synthesis reaction with aliphatic and cyclic 1,3-diene hydrocarbons [1, 2]. In the case of unsymmetrical dienes, the condensation proceeds in agreement with the electronic configuration of the components: piperylene gives mainly o-methyldihydrobenzaldehyde, isoprene – p-dihydrobenzaldehyde [2]. The reaction of propargylaldehyde with diene halogen derivatives and ethers had not been investigated.

In this report we describe the experimental results of propargylaldehyde condensation with 2-halogeno- and 2-alkoxybutadienes-1,3. The reaction was carried out in toluene at 80-120° in sealed glass tubes.

In the condensation of propargylaldehyde with 2-fluoro-, 2-chloro- and 2-bromobutadienes, the expected parahalogenodihydrobenzaldehydes were obtained in all cases. p-Fluorodihydrobenzaldehyde is a liquid, which solidifies when cooled with ice. Chloro- and bromodihydrobenzaldehydes are crystalline materials. It should be noted that the corresponding aromatic aldehydes are also crystalline materials [3], while their tetrahydro derivatives are liquids under normal conditions [4].

Semicarbazones, p-nitrophenylhydrazones and 2,4-dinitrophenylhydrazones were prepared for all three aldehydes. The melting points of these derivatives are given in Table 1.

The structure of the halogenodihydrobenzaldehydes was proved in the following way.

1. When heated with maleic anhydride in a benzene solution they did not give condensation products and, therefore, did not contain a conjugated system of double bonds.

2. All three aldehydes gave the corresponding 4-halogenobenzoic acids when oxidized with dilute nitric acid. These acids had very slightly lower melting points than those given in the literature for parahalogenobenzoic acids and therefore they could contain only a small trace of meta isomers. The latter have considerably lower melting points than the para isomers [3].

A very small amount of a second crystalline product was obtained by condensation of propargylaldehyde with 2-bromobutadiene, and this product, like the main one, also gave p-chlorobenzoic acid when oxidized. We presume that the appearance of this second product was due to the nonplanar structure of the 1,4-cyclohexadiene ring.

In this way it was established that condensation of propargylaldehyde with 2-halogenobutadienes results mainly in the formation of para-halogen-$\Delta^{1,4}$-dihydrobenzaldehydes, i. e. in agreement with the electronic configuration of the components. Probably, meta isomers are also formed simultaneously but in very small amounts. The same orientation is found in reactions of 2-halogenobutadienes with the ethylene analogue of propargylaldehyde – acrolein [4], as well as with other α,β-unsaturated acetylenic carbonyl compounds [4, 5].

The corresponding secondary 4-halogenodihydrophenylethyl alcohols were obtained by treating the parahalogenodihydrobenzaldehydes with methylmagnesium iodide. These are viscous liquids that turn brown in contact with air and their constants are given in Table 2.

The changes in boiling points and specific gravities in transition from the unsubstituted alcohol to its para-halogen derivatives are not unique. A strong decrease in the refractive index is quite noticeable when a fluorine atom is introduced into the alcohol molecule. All the halogenodihydrophenylethyl alcohols obtained by us have somewhat smaller molecular refraction values than those calculated. This is further confirmation of their 1,4-diene structure (absence of exhalation). In comparison with aromatic alcohols of similar structure, they have higher boiling points and lower refractive indices.

Para-halogenodihydrophenylethyl alcohols undergo dehydration. Unsubstituted alcohols with the same structure readily split off water when distilled with a 10% oxalic acid solution [1, 2]. Dehydration proceeded very slowly with oxalic acid and therefore more drastic conditions had to be adopted.

Dehydration with acetic anhydride at 180-200° caused isomerization with double-bond transfer and, as a result, parahalogenoethylbenzenes were formed as the main reaction products. The latter were oxidized with dilute nitric acid under pressure and the corresponding para-halogenobenzoic acids were thus obtained. These experiments provided additional confirmation of the structure of the starting materials.

Thus, the results of this investigation established that propargylaldehyde may be used for the synthesis of hydroaromatic halogen derivatives of the 1,4-cyclohexadiene series.

Mixtures of a crystalline (mainly) and liquid material were obtained by condensation of propargyl aldehyde with 2-methoxy- and 2-ethoxybutadienes-1,3. The melting points of the crystalline materials are given in Table 1. The presence of two forms of the aldehyde is probably due to the nonplanar structure of the cyclohexadiene ring.

The structure of the condensation products was not determined. However, these materials could be safely given the structure p-alkoxy-$\Delta^{1,4}$-dihydrobenzaldehydes by analogy with the order of alkoxyprene condensation with other carbonyl compounds which had been established previously by one of us [6] and was confirmed by recent experiments of other chemists [7].

TABLE 1

Material	Aldehyde melting point	Melting points		
		semicarbazones	p-nitrophenylhydrazones	2,4-dinitrophenylhydrazones
	Liquid	204—205°	197—198°	226°
	Liquid	204	212	248
	68—69°	196—197	200—201	243—244
	58—59	193	—	229—231
	29—32	—	172—173	—
	72—74	—	164—165	—

Alkoxydihydrobenzaldehydes become yellow rapidly and resinify on storage. Skin is colored yellow by them; they are insoluble in water and readily soluble in 5% sulfuric acid. The solution obtained turns brown rapidly and then a tar separates. The tar is apparently due to the instability of the 4-formylcyclohexadiene-2,5-one formed.

Alkoxydihydrobenzaldehydes react readily with hydrazine derivatives. The melting points of the p-nitrophenylhydrazones are given in Table 1.

EXPERIMENTAL

Condensation of propargylaldehyde with 2-fluorobutadiene. The 2-fluorobutadiene was prepared by a method described in the literature [8]. 20 ml (0.2 mole) of fluorobutadiene and 18 ml (0.2 mole) of propargylaldehyde in 20 ml of toluene (+ 0.1 g of hydroquinone) was heated in sealed glass tubes at 80° for

TABLE 2

Material	Boiling point	d_4^{20}	n_D^{20}	MR found	MR calculated
	103.5° (20mm)	0.9943	1.5068	37.15	37.53
	112—113 (20mm)	1.1100	1.4880	36.89	37.43
	122.5—123 (10mm)	1.1540	1.5248	42.12	42.40
	134—135 (10mm)	1.4400	1.5508	44.98	45.30

8 hours. The reaction products were distilled in steam. The distillation gave an oily layer of 9.6 g (42%) of p-fluorodihydrobenzaldehyde.

B. p. 89° (20 mm), d_4^{20} 1.1570, n_D^{20} 1.4960. MR 31.84. C_7H_7OF. Calc. 31.30

The semicarbazone and the nitrophenylhydrazone of this aldehyde were recrystallized from dilute ethanol, and the 2,4-dinitrophenylhydrazone from benzene. The latter two substances were fine needles. The analytical data is given in Table 3.

By oxidation of 0.5 g of the material with 25% nitric acid at 120° for 4-5 hours, we obtained p-fluorobenzoic acid with m. p. 178-179° (from water).

The literature gives m. p. 182.6° for p-fluorobenzoic acid and m. p. 123.6° for m-fluorobenzoic acid [3].

By treating fluorodihydrobenzaldehyde with a Grignard reagent under the usual conditions, we obtained a secondary alcohol in 66% yield with the constants given in Table 2. Heating the alcohol with acetic anhydride (twofold excess), with subsequent distillation of the reaction products in steam, gave a fluorohydrocarbon in 55% yield with b. p. 140-144°, d_4^{20} 0.9885, n_D^{20} 1.4802. Oxidation of this material yielded p-fluorobenzoic acid with m. p. 179°.

Literature data for p-fluoroethylbenzene [3]: b. p. 142-143°, d_0^{20} 0.967.

Condensation of propargylaldehyde with 2-chlorobutadiene. 18 g of 2-chlorobutadiene and 11 g of propargylaldehyde in 30 ml of toluene (+ hydroquinone) was heated for 6 hours at 110-120°. The reaction products were distilled in steam. We obtained 6.2 g (22%) of p-chlorodihydrobenzaldehyde with m. p. 68-69° (from aqueous methanol).

Found %: Cl 25.17. C_7H_7OCl. Calculated %: Cl 24.87.

The semicarbazone was recrystallized from aqueous methanol, the p-nitrophenylhydrazone from ethanol and the 2,4-dinitrophenylhydrazone from benzene. The latter had a low solubility. The melting points of these derivatives are given in Table 1 and the analytical data in Table 3.

Oxidation of the aldehyde with 25% nitric acid yielded p-chlorobenzoic acid with m. p. 237-238° (from water).

In the literature, m. p. 235°, 243° is given for p-chlorobenzoic acid and 158° for m-chlorobenzoic acid.

Treatment of 7 g of the aldehyde with methylmagnesium iodide gave 6.8 g (87%) of a secondary alcohol with the constants given in Table 2.

Found %: Cl 22.59. $C_8H_{11}OCl$. Calculated %: Cl 22.35.

By heating 6 g of the alcohol with acetic anhydride at 180-200° for 6 hours, we obtained 2.4 g of a chlorohydrocarbon.

B. p. 184-186°, d_4^{20} 1.0478, n_D^{20} 1.5215.

Found %: Cl 25.51. C_8H_9Cl. Calculated %: Cl 25.22.

Literature data for p-chloroethylbenzene [9]: b. p. 184.4°, d_4^{20} 1.0455, n_D^{20} 1.5175.

The small differences in the constants are due to traces of vinylcyclohexadiene hydrocarbons. After heating with maleic anhydride, the unreacted hydrocarbon had a closer refractive index (n_D^{20} 1.5190).

Oxidation of the chlorohydrocarbon with 25% nitric acid gave p-chlorobenzoic acid with m. p. 238°.

Condensation of propargylaldehyde with 2-bromobutadiene. 10.5 g (0.2 mole) of propargylaldehyde and 14 g (0.1 mole) of bromoprene in 30 ml of toluene (+ hydroquinone) were heated at 120° for 6 hours. The mixture was worked up in the usual way to give 15.7 g (80%) of bromodihydrobenzaldehyde with m. p. 58-59°. In the recrystallization of the crude product from methanol, we isolated 0.7 g of a substance with m. p. 42-43°.

Substance with m. p. 58-59°.

Found %: Br 42.54, 42.80. C_7H_7OBr. Calculated %: Br 42.73.

By oxidizing the substance with 25% nitric acid, we obtained p-bromobenzoic acid with m. p. 248-249°.

In the literature, m. p. 251-253° is reported for p-bromobenzoic acid and m. p. 155° for m-bromobenzoic acid [3].

Substance with m. p. 42-43°.

Found %: Br 42.87. C_7H_7OBr. Calculated %: Br 42.73.

Oxidation of the material with nitric acid yielded only p-bromobenzoic acid with the same m. p.

In further experiments, we used only the material with m. p. 58-59°.

The semicarbazone, p-nitrophenylhydrazone and 2,4-dinitrophenylhydrazone were prepared and recrystallized in the usual way. The analytical data are given in Table 3.

Treatment of the aldehyde with methylmagnesium bromide gave a 66% yield of a secondary alcohol. The constants are given in Table 2.

Found %: C 47.02; H 5.80; Br 39.66. $C_8H_{11}OBr$. Calculated %: C 47.31; H 5.45; Br 39.35.

Dehydration of the alcohol with acetic anhydride gave a material with b. p. 203-205°, d_4^{20} 1.3330, n_D^{20} 1.5488. Oxidation of this with nitric acid gave bromobenzoic acid with m. p. 234°.

Literature data for p-bromoethylbenzene [9]: b. p. 205°, d_4^{20} 1.3423, n_D^{20} 1.5448.

TABLE 3

Aldehyde derivatives	N content (in %)		Aldehyde derivatives	N content (in %)	
	found	calculated		found	calculated
4-Fluorodihydrobenzaldehyde			4-Bromodihydrobenzaldehyde		
Semicarbazone	23.21	22.94	Semicarbazone	17.00	17.23
p-Nitrophenylhydrazone	15.95	16.09	p-Nitrophenylhydrazone	13.30	13.05
2,4-Dinitrophenylhydrazone	18.57	18.30	2,4-Dinitrophenylhydrazone	15.61	15.26
4-Chlorodihydrobenzaldehyde			4-Methoxydihydrobenzaldehyde		
Semicarbazone	20.77	21.05	p-Nitrophenylhydrazone	15.25	15.38
p-Nitrophenylhydrazone	15.39	15.13	4-Ethoxydihydrobenzaldehyde		
2,4-Dinitrophenylhydrazone	17.60	17.37	p-Nitrophenylhydrazone	14.73	14.63

Condensation of propargylaldehyde with 2-methoxy- and 2-ethoxybutadienes. 7.7 g of propargylaldehyde and 12 g of methoxybutadiene in 40 ml of toluene was heated at 120° for 6 hours. Distillation of the reaction mixture in vacuum gave 15 g (77%) of condensation product and 2 g of tar.

B. p. 106.5-107.5° (10 mm), 122-123° (20 mm), m. p. 29-31°.

Found %: C 69.55; H 7.27. $C_8H_{10}O_2$. Calculated %: C 69.54; H 7.29.

Under the same conditions, 15 g of ethoxybutadiene and 9.5 g of propargylaldehyde yielded 16.7 g (72%) of condensation product with m. p. 72-74°.

Found %: C 71.03; H 7.59. $C_9H_{12}O_2$. Calculated %: C 71.03; H 7.95.

SUMMARY

1) The condensation of propargylaldehyde with 2-fluoro-, 2-chloro-, 2-bromo-, 2-methoxy- and 2-ethoxybutadienes-1,3 was investigated.

2) The condensation products were 4-halogeno or 4-alkoxy-$\Delta^{1,4}$-dihydrobenzaldehydes which are described.

3) The halogenodihydrobenzaldehyde structure was proved by oxidation with dilute nitric acid under pressure to form the corresponding para-halogenobenzoic acids.

4) The corresponding secondary 4-halogeno-$\Delta^{1,4}$-dihydro-β-phenylethyl alcohols were obtained by treatment of the 4-halogenodihydrobenzaldehydes with methyl magnesium halides.

5) It was shown that halogen derivatives of ethylbenzene are the main product of dehydration of these alcohols.

LITERATURE CITED

[1] A. A. Petrov, J. Gen. Chem. 24, 2136 (1954) (T. p. 2107).*

[2] A. A. Petrov and N. P. Sopov, J. Gen. Chem. 25, 517 (1955) (T. p. 485).*

[3] Dictionary of Organic Compounds (Foreign Lit. Press, 1949).

[4] A. A. Petrov and N. P. Sopov, J. Gen. Chem. 17, 1295 (1947).

[5] J. S. Meek and W. B. Trapp, J. Am. Chem. Soc. 74, 2686 (1952).

[6] A. A. Petrov, J. Gen. Chem. 11, 661 (1947); 17, 538 (1947); A. A. Petrov and M. G. Vladimirova, J. Gen. Chem. 17, 1543 (1947).

[7] A. A. Petrov, Progr. Chem. 21, 452 (1952).

[8] American Patent No. 2437308; C. A. 42, 4192 (1948); American Patent No. 2437148; C. A. 42, 4193 (1948); English Patent No. 580910; C. A. 41, 2428 (1947); 590381; C. A. 42, 334 (1928).

[9] R. R. Dreisbach and R. A. Martin, Ind. Eng. Chem. 41, 2875 (1949).

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*T. p. = C. B. Translation pagination.

TRANSFORMATIONS OF PINACONES CONTAINING SUBSTITUTED ACETYLENIC RADICALS

XIII. THE ACTION OF MERCURY SALTS ON UNSYMM. METHYL-DIPHENYL-PHENYLETHYNYL-ETHYLENE GLYCOL AND ON TRIMETHYLPHENYLETHYL-PHENYLETHYNYL-ETHYLENE GLYCOL

E. D. Venus-Danilova and A. Fabritsy

Continuing the study of transformations of ditertiary α-glycols of the acetylenic series (pinacones containing substituted acetylenic radicals) under the influence of salts of mercury, we have investigated and now describe the action of mercuric chloride and acetate on unsymm. methyl-diphehyl-phenylethynyl-ethylene glycol (2-methyl-1,1,4-triphenylbutyne-3-diol-1,2) (II) and of mercuric chloride on trimethyl-phenylethynyl-ethylene glycol (2,3-dimethyl-5-phenylpentyne-4-diol-2,5) (I).

It was previously found that the action of mercuric chloride on unsymm. dimethyl-phenyl-phenylethynyl-ethylene glycol leads to the mercury complex salt of 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 [1,2].

In the case of unsymm. dimethyl-phenyl-tert.-butylethynyl-ethylene glycol, the corresponding complex mercury salt was also obtained [3]; its composition was $(glycol\text{–}OH)^{+}HgX_3^{-} \cdot H_2O$.

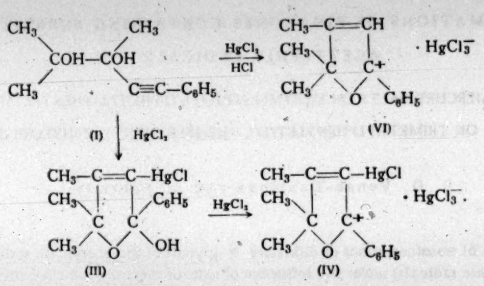
Unsymm. methyl-diphenyl-phenylethynyl-ethylene glycol is an interesting substance because, unlike the pinacones with substituted acetylenic radicals previously studied [4], it does not isomerize under the action of sulfuric acid to a substituted 2-hydroxydihydrofuran-2,5 and does not give fission products of the corresponding olefinic γ-ketoalcohols (opened forms of 2-hydroxydihydrofurans-2,5), and in consequence of the pinacoline rearrangement, it is transformed into a ketone of the acetylenic series [5]. It could therefore be expected that in presence of mercuric chloride, the glycol would undergo a different transformation than that of unsymm. dimethyl-phenyl-phenylethynyl-ethylene glycol.

Treatment of trimethyl-phenylethynyl-ethylene glycol [6] with sulfuric acid previously gave a ketone of the acetylenic series and the unstable 2-hydroxydihydrofuran which only exists in acid solution in the form of the sulfate. It was therefore of interest to examine the possibility of formation from this glycol of a complex mercury salt of the isomeric 4,5,5-trimethyl-2-phenyl-2-hydroxydihydrofuran-2,5.

Reaction of equimolar amounts of trimethyl-phenylethynyl-ethylene glycol (I) and mercuric chloride in ethyl alcohol with heating, i.e. under the conditions previously applied for unsymm. dimethyl-phenyl-phenylethynyl- and dimethyl-tert.-butylethynyl-ethylene glycols [1,3], could not be stopped at the stage of formation of the complex salt. The initially formed precipitate quickly darkened and then dissolved. From the ethereal extract was isolated a noncrystallizing dark resin which solidified on standing to a dark, stiff mass not containing mercury and having twice the molecular weight of the glycol.

Further experiments on the reaction of the glycol with mercuric chloride in alcohol were performed with cooling. In this manner a yellow, finely crystalline substance quickly came down and had the empirical formula $C_{13}H_{14}OCl_4Hg_2$, which corresponded to the structure of the anhydrous complex mercury salt of mercurated 4,5,5-trimethyl-2-phenyl-2-hydroxydihydrofuran-2,5 (IV). Formation of this compound can be represented by the same scheme as for the transformation of unsymm. dimethyl-phenyl-phenylethynyl-ethylene glycol under the action of mercuric chloride [1], i.e. by the addition of mercuric chloride at the triple bond of the glycol, followed by rearrangement and loss of hydrogen chloride. The resultant mercurated 2-hydroxydihydrofuran-2,5 (III) forms

with mercuric chloride a complex salt which contains a mercurated cation (IV). Evidently, unlike unsymm. dimethyl-phenyl-phenylethynyl-ethylene glycol, trimethyl-phenylethynyl-ethylene glycol adds on mercuric chloride and subsequently rearranges many times faster in comparison with the isomerization of the glycol to 4,5,5-trimethyl-2-phenyl-2-hydroxydihydrofuran-2,5. It is even possible that the formation of the 2-hydroxy-dihydrofuran-2,5 does not in general take place, since compound (IV) is the sole reaction product, and its yield reaches 90%.



Reaction of trimethyl-phenylethynyl-ethylene glycol with mercuric chloride in presence of hydrochloric acid, with cooling, gave a white crystalline substance with the empirical formula $C_{13}H_{15}OCl_3Hg$, which is the complex mercury salt of 4,5,5-trimethyl-2-phenyl-2-hydroxydihydrofuran-2,5 (V). Evidently, the excess of hydrochloric acid decomposes the mercury-containing cation with replacement of an HgCl residue by hydrogen.

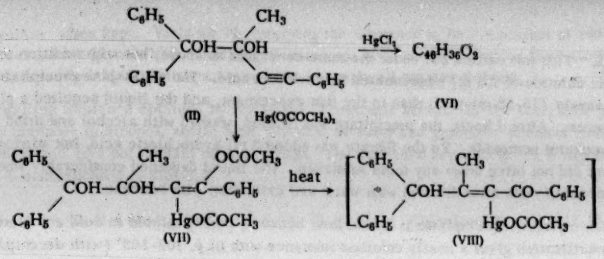
The reaction between unsymm. methyl-diphenyl-phenylethynyl-ethylene glycol (II) and mercuric chloride, when carried out in alcoholic solution with equimolar amounts of reactants with gentle heating, is accompanied by separation of a yellowish, amorphous precipitate which, after purification, did not contain either mercury or chlorine and did not give a reaction for the hydroxyl group. Its empirical formula is $C_{46}H_{36}O_2$ (VI). Its structure was not established. It is probably formed from two molecules of glycol and with loss of two molecules of water.

It is interesting to note that trimethyl-phenylethynyl-ethylene glycol, which also contains a methyl group at the carbon atom linked to the phenylacetylene residue, likewise forms a condensation product when treated with mercuric chloride while the mixture is heated.

Mercuric acetate, unlike mercuric chloride, does not bring about dimerization and dehydration of unsymm. methyl-diphenyl-phenylethynyl-ethylene glycol (II), but gives unstable organomercury compounds. The difference in the effects of the two mercury salts is due to mercuric acetate being a strongly mercurating substance which very easily adds on at the triple bond. In this case, the reaction is similar to that of unsymm. dimethyl-phenyl-phenylethynyl-ethylene glycol, which also gave an organomercury compound [7], but a much more stable one, when treated with mercuric acetate.

In the case of unsymm. methyl-diphenyl-phenylethynyl-ethylene glycol, however, with application of heat, it was impossible to isolate any pure products of reaction. The analytical data indicate that all the substances prepared were mixtures of organomercury compounds with other substances – possibly dimer or a product of its mercuration.

Reaction of glycol (II) with mercuric acetate in alcoholic solution in the cold leads to separation of a white crystalline substance which is the product of addition of mercuric acetate at the triple bond of the glycol (VII). The correctness of this structure is supported to some extent by the difficult solubility of the product in organic solvents. Products of addition of mercury salts at the triple bond possess the properties of quasi-complex compounds [8], and a complex structure frequently brings about a sharp drop in solubility.



The analytical data of the product with the proposed structure (1,1,4-triphenyl-2-methyl-3-acetomercuri-4-acetoxy-buten-3-diol-1,2) (VII) are not altogether satisfactory because the substance cannot be recrystallized due to its insolubility, and a slight trace of mercuric acetate would alone suffice to give a higher result for the mercury content (as was observed).

Heating of the white crystalline substance converts it into a transparent glassy mass, readily soluble in all organic solvents. This glassy mass is formed when the glycol is reacted hot with mercuric acetate in acetic acid or alcohol. This product contains mercury, gives a reaction for the hydroxyl group, and forms a yellow-red mercury-containing precipitate with 2,4-dinitrophenylhydrazine.

The glassy product is probably a mercurated ketol (VIII), formed from the organomercury compound (VII) by isomerization according to the scheme that we previously [1,7] put forward, or as a result of hydrolysis of the enol (VII). This hypothesis cannot, however, be considered fully proved, since the analyses of this product and of the corresponding 2,4-dinitrophenylhydrazone do not give satisfactory results (values for mercury and carbon 1-5% too low). The substance is very unstable and is even modified by the action of water. Attempts to replace the acetyl residue in this substance by halogen by the action of an alcoholic solution of calcium chloride, or to prepare a symmetrization product from it, were unsuccessful.

EXPERIMENTAL

1. Trimethyl-phenylethynyl-ethylene Glycol

Experiment 1. The reaction was carried out in solution in 95% ethyl alcohol (10-fold excess in relation to the glycol) with equimolar amounts of glycol and mercuric chloride (5 g glycol with b.p. 150-151° at 5 mm, and 6.6 g mercuric chloride). The separately prepared solutions of glycol and mercuric chloride were previously cooled (ice and water). The mixture turned cloudy about a minute after the solutions were mixed, while cooling, and 7.3 g of yellowish crystalline precipitate came down; this was filtered after an hour, washed several times with alcohol, and dried in a vacuum desiccator over phosphorus pentoxide. Stirring of the filtrate for two hours at the normal temperature brought down another 0.6 g of the same substance. After separation of the crystals, the alcoholic solution was diluted with ten times the amount of water and extracted with benzene. The benzene was evaporated to leave a small quantity of uncrystallizable substance not containing mercury and insoluble in acids. Analysis showed that the aqueous alcoholic solution, after extraction with benzene, contained only 0.02% HgS (analyzed as HgS); consequently, all of the mercuric chloride had entered into reaction.

The prepared yellow, crystalline substance is insoluble in benzene, sparingly soluble in cold alcohol, better soluble in hot alcohol. It readily decomposes with blackening when heated, which hinders its recrystallization. It contains mercury and chlorine, does not give a reaction for hydroxyl groups, does not exhibit fluorescence with strong sulfuric acid, and does not melt but darkens at 135° and decomposes at 145°. Yield 89.0% on the mercuric chloride, the assumption that the substance is the mercury complex salt – 4,5,5-trimethyl-2-phenyl-3-chloro-mercuri-2-hydroxydihydrofuran-2,5 (IV).

Found %: C 21.00; H 1.98; Hg 55.26; Cl 19.52, 19.33. $C_{13}H_{14}OCl_4Hg_2$. Calculated %: C 21.39; H 1.92; Hg 55.02; Cl 19.47.

Experiment 2. This was carried out under the same conditions as above, but with addition to the alcoholic solution of mercuric chloride of 2.5 ml concentrated hydrochloric acid. The white-pink precipitate began to separate out more slowly (10-15 minutes) than in the first experiment, and the liquid acquired a pink-raspberry color during the process. After 2 hours, the precipitate was filtered, washed with alcohol and dried in a vacuum desiccator over phosphorus pentoxide. To the filtrate was added 3 ml hydrochloric acid, but stirring for 2 hours at room temperature did not bring down any more substance. The liquid darkened considerably when heated, and yielded a small amount of resin after dilution with water and extraction with benzene.

The light pink crystalline precipitate is insoluble in benzene, poorly soluble in cold and more soluble in hot alcohol. Recrystallization gives a nearly colorless substance with m.p. 102-103° (with decomp.). The substance easily dissolves in acids without coloration; it contains mercury and chlorine; hydroxyl was not detected.

Yield 8 g or 66% on the glycol, assuming that the substance is the complex mercury salt of 4,5,5-trimethyl-2-phenyl-2-hydroxydihydrofuran-2,5 (V).

Found %: C 31.22; H 2.65; Hg 40.75; Cl 21.51. $C_{13}H_{15}OCl_3Hg$. Calculated %: C 31.57; H 3.04; Hg 40.59; Cl 21.55.

2. Unsymm. Methyl-diphenyl-phenylethynyl-ethylene Glycol

Experiment 1. Glycol and mercuric chloride. Slight yellowing quickly occurred when 15 ml of an alcoholic solution of glycol (3 g, m.p. 120°) was mixed with 15 ml of an alcoholic solution of mercuric chloride (2.5 g) at the ordinary temperature; subsequent heating for half an hour at 50°, with stirring, led to separation of a white precipitate which later turned brown. After the reaction mass was heated for 5 hours and stood for 24 hours at the ordinary temperature, the precipitate was filtered, washed with alcohol and dried in the air. The filtrate contained mercuric chloride and a small quantity of resin (after extraction with ether).

After 3 purifications of the amorphous precipitate by precipitation from acetone solution with alcohol, a barely yellow substance was obtained with m.p. (unsharp) 110-123°. It is nearly insoluble in methyl and ethyl alcohol, poorly soluble in gasoline, readily soluble in ether, benzene and acetone, and separates from all the solvents in the form of a pale yellow light powder. It does not react with strong hydrochloric acid; with sulfuric acid it gives a dark brown color without fluorescence. In a medium of aqueous pyridine it decolorizes permanganate and a solution of bromine in chloroform. It does not contain halogen, mercury or hydroxyl groups. Since the substance does not dissolve either in alcohol or acetic acid, an experiment with 2,4-dinitrophenylhydrazine could not be carried out.

Found %: C 89.21, 89.32; H 5.90, 6.04. M 618. $C_{46}H_{36}O_2$. Calculated %: C 89.03; H 5.83. M 620.

The analytical data indicate that the substance was formed from two molecules of glycol with splitting-off of two molecules of water.

The substance was oxidized in aqueous pyridine with potassium permanganate in the calculated amount equivalent to 16 atoms of active oxygen per mole of substance (3.1 g substance and 8.7 g permanganate) in the cold. By the usual method benzoic acid and benzophenone were separated; a small amount of starting substance was recovered. Oxidation went very slowly and foaming occurred at the start. Use of a smaller quantity of oxidizing agent (8 atoms active oxygen per mole substance) with heating to about 50°, likewise gave benzophenone and benzoic acid and part of the original substance. Oxidation evidently goes with difficulty at the start, but the intermediate products formed are then oxidized very quickly.

The amorphous product obtained was not examined more closely.

Experiment 2. Glycol and mercuric acetate. In view of the fact that a homogeneous substance was not obtained by heating in acetic acid or alcoholic solution, the reaction of the glycol with mercuric acetate was conducted at the normal temperature. 5 g glycol was treated with 4.8 g mercuric acetate (equimolar amounts) and the solvent was 30 ml 90% alcohol. A white precipitate began to come down a few minutes after the solutions of reactants had been mixed; after 3 hours' stirring the precipitate was filtered, washed with alcohol, water and again with alcohol, and dried in a vacuum-desiccator. 2.6 g of colorless crystalline substance was obtained

which turned yellow when kept. Yield 66.7%, assuming the substance to be the product of addition of mercuric acetate to the acetylenic glycol (VII). It readily decomposes when recrystallization from alcohol is attempted, forming a solid, amorphous dark yellow mass, soluble in nearly all organic solvents.

The crystalline substance obtained by the action of mercuric acetate on the acetylenic glycol at room temperature is insoluble in alcohol, acetic acid, acetone, benzene and gasoline. It reacts violently with methylmagnesium iodide and does not contain ethoxyl groups. The substance is probably 1,1,4-triphenyl-2-methyl-3-acetomercuri-4-acetoxybuten-3-diol-1,2.

Found %: C 50.65; H 4.05; Hg 33.64; OH 6.04. $C_{27}H_{26}O_6Hg$. Calculated %: C 50.11; H 4.02; Hg 31.03; OH 5.26.

The high analytical value for mercury is the result of slight contamination with mercuric acetate.

SUMMARY

1. Reaction of unsymm. trimethyl-phenylethynyl-ethylene glycol with mercuric chloride in alcoholic solution in the cold gives a complex salt of 4,5,5-trimethyl-2-phenyl-3-chloromercuri-2-hydroxydihydrofuran-2,5 with mercuric chloride ($C_{13}H_{14}OHgCl \cdot HgCl_2$). In presence of a small amount of hydrochloric acid, the reaction leads to the complex salt of 4,5,5-trimethyl-2-phenyl-2-hydroxydihydrofuran-2,5 with mercuric chloride ($C_{13}H_{15}O \cdot HgCl_2$).

2. Unsymm. methyl-diphenyl-phenylethynyl-ethylene glycol reacts with mercuric chloride with removal of two molecules of water and with formation of a dimer of the glycol free from mercury or chlorine.

3. With mercuric acetate, unsymm. methyl-diphenyl-phenylethynyl-ethylene glycol gives an unstable product of addition of mercuric acetate at the triple bond of the glycol.

LITERATURE CITED

[1] E. D. Venus-Danilova and A. Fabritsy, J. Gen. Chem. 26, 1609 (1956) (T.p. 1803).*

[2] E. D. Venus-Danilova and A. Fabritsy, J. Gen. Chem. 26, 884 (1956) (T.p. 1007).*

[3] E. D. Venus-Danilova et al., J. Gen. Chem. 26, 1160 (1956) (T.p. 1317).*

[4] E. D. Venus-Danilova et al., Trans. Leningrad Inst. Tech., 1954, No. 30, 38.

[5] E. D. Venus- Danilova et al., J. Gen. Chem. 19, 951 (1949)(T.p. 941).*

[6] E. D. Venus-Danilova and V. I. Serkova, J. Gen. Chem. 21, 2211 (1951) (T.p. 2477).*

[7] E. D. Venus-Danilova and A. Fabritsy, J. Gen. Chem. 26, 1901 (1956) (T.p. 2119).*

[8] L. G. Makarova and A. N. Nesmeyanov, Synthetic Methods in the Field of Organometallic Compounds of Mercury (Acad. Sci. USSR Press, 1945), 53.

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*T. p. = C. B. Translation pagination.

DERIVATIVES OF ALKYLPHOSPHINOUS AND DIALKYLPHOSPHINIC ACIDS

IV. ADDITION AND ISOMERIZATION REACTIONS OF ESTERS OF ALKYLPHOSPHINOUS ACIDS

A. Razumov and O. Mukhacheva

Prior to studies published in 1952 [1,2], esters of alkylphosphinous acids had not been mentioned in the literature. In our papers [1,3] we reported the synthesis of esters of ethyl-, n-propyl-, n-butyl- and isobutylphosphinous acids. In the present paper we report some of their properties.

Esters of alkylphosphinous acids possess a series of interesting properties, in particular, a great facility for diverse reactions of addition and isomerization. This enables fairly easy transition from esters to other derivatives of alkylthiophosphinous, selenophosphinous and dialkylphosphinic acids, some of which possess interesting biological properties. Additions and isomerizations of esters of phosphorous and arylphosphinous acids have been studied fairly extensively [4,5], whereas similar esters of alkylphosphinous acids have hardly been studied. Prior to publication of the above mentioned papers [1,2], only a single case of addition of sulfur to an ester of amylphosphinous acid was known [6]. The addition product was not very pure and was not well characterized. Addition of sulfur to esters of alkylphosphinous acids goes with very much greater facility than the addition to esters of phosphorous and phenylphosphinous acids. We have attempted to explain this phenomenon in one of our earlier papers [1].

Addition of sulfur to the synthesized esters of alkylphosphinous acids was effected either in benzene solution or in the absence of solvent. The reaction is always accompanied by considerable heat development. Six esters of alkylthiophosphinic acids were obtained (Table 1) by sulfur addition reactions.

TABLE 1*

Formula	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Content (%) S calculated	S found	P calculated	P found	Yield (%)
$C_2H_5P(S)(OC_2H_5)_2$	86.5—87 (12)	1.0349	1.4617	48.32	48.26	17.58	17.79, 17.64	—	—	80
n-$C_3H_7P(S)(OC_2H_5)_2$	60—62 (0.4)	1.0177	1.4615	52.90	52.88	16.33	16.27, 16.40	15.82	16.06, 16.05	81
n-$C_3H_7P(S)(OC_3H_7\text{-}n)_2$	87—88 (0.24)	0.9871	1.4608	62.25	62.12	14.29	14.40, 14.27	13.83	13.97, 13.94	75
n-$C_4H_9P(S)(OC_2H_5)_2$	77—78 (1.0)	1.0027	1.4634	57.72	57.50	—	—	14.77	14.66, 14.78	78
n-$C_4H_9P(S)(OC_3H_7\text{-}n)_2$	137.5—139 (15)	0.9791	1.4620	66.83	66.74	—	—	13.03	13.09, 13.21	76
n-$C_4H_9P(S)(OC_4H_9\text{-}n)_2$	109—111 (0.3)	0.9649	1.4615	75.76	75.97	—	—	11.65	11.72, 11.80	71

* The first substance listed in the table was also prepared by B. A. Arbuzov and N. I. Rizpolozhensky [7]. The constants of our synthesized product differ slightly from those obtained by them. Agreement between the found and calculated MR_D in both cases is good. We took the usually accepted value of AR_S 9.7 [8,9].

We also obtained the esters of alkylthiophosphinic acids by another route, namely via the corresponding acid chlorides of the composition $RP(S)Cl_2$, a method that we had developed previously [1]. The esters of alkylthiophosphinic acids are nearly insoluble in water, so that the study of their biological properties is made difficult. It is interesting that all the ethyl esters of the prepared acids possess a pleasant and refreshing, grassy odor, whereas the propyl and butyl esters of the same acids have an unpleasant garlic-onion odor.

Selenium was added onto esters of alkylphosphinous acids in a similar manner to sulfur, and the previously unknown esters of alkylselenophosphinic acids were obtained. Addition of selenium was realized under the same conditions, and the reaction is likewise exothermic. Not all the selenium could be brought into combination, even with heating. We account for this by the presence of tellurium in the selenium (the selenium was 96-98% pure). The prepared esters of alkylselenophosphinic acids are listed in Table 2.

The literature contains no data for the magnitude of the atomic refraction of selenium linked to the double bond with phosphorus. We calculated this magnitude for the esters of alkylselenophosphinic acids. The mean value of AR_{Se} is 13.38. As we see from the data of Table 2, there is good agreement between the values of AR_{Se} of the esters that we synthesized (maximum deviation from the mean value $\pm$ 0.2). It was of interest to compare the atomic refraction for selenium in other classes of selenium-containing organic compounds of phosphorus. This could not, however, be done; very few selenium-containing organophosphorus compounds are known, and of these the authors do not give the physical constants required for the calculation. The selenides of tertiary phosphines reported in the literature likewise cannot be used for this purpose since they are crystalline substances.

TABLE 2

Formula	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR_D found	AR_{Se}	Content (in %)				Yield (%)
						Se		P		
						calculated	found	calculated	found	
$C_2H_5P(Se)(OC_2H_5)_2$	97.5 (11.0)	1.2743	1.4872	51.73	13.17	34.49	34.20, 33.82	13.53	13.61, 13.69	75
n-$C_3H_7P(Se)(OC_2H_5)_2$	74—76 (0.65)	1.2316	1.4855	56.63	13.45	—	—	12.75	12.71, 12.52	75
n-$C_3H_7P(Se)(OC_3H_7\text{-}n)_2$	95—96 (0.28)	1.1696	1.4813	66.02	13.60	29.15	29.06, 28.99	11.43	11.31, 11.27	72
n-$C_4H_9P(Se)(OC_2H_5)_2$	90—91.5 (0.4)	1.2007	1.4850	61.39	13.59	—	—	11.97	11.99, 11.86	74
n-$C_4H_9P(Se)(OC_3H_7\text{-}n)_2$	112—114 (0.23)	1.1547	1.4804	70.22	13.18	—	—	10.87	10.63, 10.57	65
n-$C_4H_9P(Se)(OC_4H_9\text{-}n)_2$	115—116 (0.27)	1.1129	1.4775	79.61	13.34	25.24	25.09, 25.03	—	—	73

Esters of alkylselenophosphinic acids are strongly refracting liquids with a weak odor and very poor solubility in water. They deposit free selenium on standing in the air, even in sealed ampoules. When the air is replaced by carbon dioxide (in sealed ampoules), the esters can be kept unchanged for a very long time (at least one year).

Apart from sulfur and selenium, the esters of alkylphosphinous acids add on copper monohalides to form crystalline products in some cases and syrupy liquids in others, as shown in Table 3.

It is interesting to note that the melting point of the products falls with increasing complexity of composition, and that the more complex substances are not crystalline, but form oils.

Esters of alkylphosphinous acids, containing trivalent phosphorus, readily isomerize under the influence of compounds with a labile halogen. Isomerization of these esters goes very much faster than that of esters of phosphorous or arylphosphorous acids. We have given an explanation of this phenomenon [1].

A few experiments on the isomerization of esters of alkylphosphinous acids under the influence of various compounds, containing a labile halogen, have been described in the last 2 or 3 years [1, 2]. Some of the esters

TABLE 3

Formula	Melting point	Phosphorus content (%)	
		found	calculated
$C_2H_5P(OC_2H_5)_2 \cdot CuI$	167—167.5	9.16, 9.13	9.10
$n\text{-}C_3H_7P(OC_2H_5)_2 \cdot CuI$ . . .	140—140.5	8.92, 8.82	8.74
$n\text{-}C_3H_7P(OC_3H_7\text{-}n)_2 \cdot CuI$ . .	92—93	8.15, 8.24	8.10
$n\text{-}C_4H_9P(OC_2H_5)_2 \cdot CuI$ . .	Oil	—	—
$n\text{-}C_4H_9P(OC_3H_7\text{-}n)_2 \cdot CuI$ . .	Ditto	—	—
$n\text{-}C_4H_9P(OC_4H_9\text{-}n)_2 \cdot CuI$ . .	"	—	—

TABLE 4

Formula	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Yield (%)
$(C_2H_5)_2P(O)OC_2H_5$	88—88.5 (10)	0.9908	1.4337	39.43	39.65	80
$(n\text{-}C_3H_7)_2P(O)OC_3H_7\text{-}n$ . .	95—97 (0.4)	0.9447	1.4386	53.42	53.51	83
$(n\text{-}C_4H_9)_2P(O)OC_4H_9\text{-}n$ . .	106—107 (0.2)	0.9269	1.4446	67.14	67.36	78

of ethyl-, n-propyl- and n-butylphosphinous acids that we synthesized were isomerized to the esters of the corresponding dialkylphosphinic acids (Table 4).

The first of the above products was synthesized simultaneously by B. A. Arbuzov and N. I. Rizpolozhensky [2], while the third was obtained by another route by G. Kosolapov [10].

The esters were isomerized either by the known method in sealed tubes or by heating in a flask with a high-duty condenser in a stream of nitrogen or carbon dioxide. A short induction period was observed during isomerization in the flask, after which a violent reaction set in with considerable heat development, so that heating was not required. Isomerization of esters of alkylphosphinous acids must be conducted under more or less strict temperature control, since prolongation of the heating period or unnecessary raising of the temperature lead to decomposition of the ester, and the corresponding acids are then obtained instead of esters of alkylphosphinic acid. Thus, the isomerization of the n-butyl ester of n-butylphosphinous acid in presence of butyl iodide at 110° gave results different from those at 150°, in each case with heating for 4 hours. In the first case, only the normal product was obtained, whereas in the second case, 63% of the normal product and 15% of the corresponding acid were obtained. Similar differences with esters of phosphorous acid were only observed in rare cases, most frequently when the ester contained a secondary radical [11-13].

EXPERIMENTAL

Synthesis of the diethyl ester of ethylphosphinic acid. A stream of carbon dioxide or nitrogen was passed into a three-necked flask fitted with condenser, thermometer and stirrer, and 24.5 g ethyl ester of ethylphosphinous acid and 100 ml anhydrous benzene were introduced, followed portion-wise by 5.2 g finely pulverized sulfur. The reaction was conducted at a temperature not above 60°, which was regulated by the addition of sulfur in small portions. The product was then fractionated. All the other esters of alkylthiophosphinic acids were obtained in a similar fashion.

Synthesis of ethyl ester of ethylselenophosphinic acid. A stream of carbon dioxide or nitrogen was passed into a three-necked flask fitted with condenser, stirrer and thermometer, and 15 g ethyl ester of ethylphosphinous acid was charged in. To the ester was added, portion-wise, 7.9 g of finely pulverized metallic selenium.

The temperature rose to 95°. After the whole of the selenium had been added, the flask was heated 1 hour at 110-120°, the unreacted selenium was filtered off (0.12 g), and the product fractionated. All the remaining esters of alkylselenophosphinic acids were obtained in similar fashion.

Preparation of complex compounds from esters of alkylphosphinous acid and cuprous iodide. 3.4 g of diethyl ester of ethylphosphinous acid was placed in a small flask, fitted with a thermometer and a gas discharge tube, and 5.3 g of cuprous iodide was added. The temperature of the reaction mixture rose from 19 to 81°. The residue of copper salt was dissolved by carefully heating the product to 130°. On cooling, the whole mass crystallized. The crystals were dissolved in methyl alcohol, and the solution filtered from the very small residue. After recrystallization from anhydrous methyl alcohol, the first product had m.p. 167-167.5° (Table 1). All the other products were prepared in similar fashion.

Isomerization of esters of alkylphosphinous acids. Isomerization was effected either in sealed tubes or in specially designed, all-glass apparatus. A 250-ml flask was joined by a ground-glass connection to a 2-branch adapter, one end of which fitted into a condenser and the other into a gas exit tube. Into the flask were charged 90 g diethyl ester of ethylphosphinous acid and 96 g ethyl iodide; a stream of nitrogen (freed from oxygen) or carbon dioxide was passed into the flask. With cautious heating, the liquid at first turned slightly cloudy, and then became colored. When the temperature in the flask reached 72°, the reaction mass boiled up violently and the temperature rose to 135°. Violent boiling continued for 15-20 minutes. During this period the heating was stopped, but was afterwards resumed for 2-2½ hours (until the odor of the original substance had disappeared). The condenser was then put in the sloping position and the ethyl iodide was distilled off. The residue was twice fractionated for isolation of the ethyl ester of diethylphosphinic acid. Isomerization of the other compounds was effected in similar fashion.

SUMMARY

1. The addition of sulfur, selenium and cuprous iodide to esters of ethylphosphinous, n-propylphosphinous and n-butylphosphinous acids was studied.

2. Synthesis of previously unknown esters of alkylthiophosphinic acids, of esters of alkylselenophosphinic acids and of complex compounds of esters of alkylphosphinous acids with cuprous iodide was accomplished.

3. Isomerization of esters of ethylphosphinous, n-propylphosphinous and n-butylphosphinous acids was investigated.

4. The isomerization studies led to synthesis of some previously known and some previously unknown esters of dialkylphosphinic acids.

5. The value of the atomic refraction of selenium in esters of alkylselenophosphinic acids is estimated.

LITERATURE CITED

[1] A. I. Razumov et al., Bull. Acad. Sci. USSR 1952, 894 (T.p. 797).*

[2] B. A. Arbuzov and N. I. Rizpolozhensky, Bull. Acad. Sci. USSR 1952, 854 (T.p. 765).*

[3] A. Razumov and O. Mukacheva, J. Gen. Chem. 26, 1436 (1956) (T.p. 1615).*

[4] A. E. Arbuzov, Selected Works (Acad. Sci. USSR Press, 1952).

[5] B. A. Arbuzov, Reactions and Methods of Investigation of Organic Compounds (State Chem. Press, 1954).

[6] F. Guichard, Ber. 32, 1577 (1899).

[7] B. A. Arbuzov and N. I. Rizpolozhensky, Bull. Acad. Sci. USSR 1952, 854 (T.p. 765).*

[8] M. I. Kabachnik, Bull. Acad. Sci. USSR 1948, 219.

* T.p. = C. B. Translation pagination.

[9] B. Boudet and R. Ramband, Bull. Soc. Chim. 1948, 793.

[10] G. Kosolapoff, J. Am. Chem. Soc. 76, 5466 (1951).

[11] A. E. Arbuzov and I. A. Arbuzova, J. Russ. Chem. Soc. 61, 1905 (1929).

[12] A. E. Arbuzov et al., J. Gen. Chem. 15, 766 (1945).

[13] A. E. Arbuzov and F. G. Valitova, Bull. Acad. Sci. USSR 1952, 801.

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CYCLIC ESTERS OF ETHYLARSINOUS ACID

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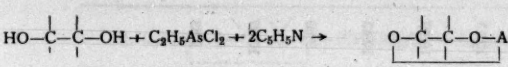
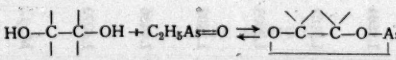
Esters of alkylarsinous acids of the general formula Alk As$(OR)_2$ have been little studied [1]. Cyclic esters of alkylarsinous acids have not been described at all.

The present work is a development of our investigations on cyclic esters of arsenious and arylarsinous acids [2]. We synthesized cyclic esters of ethylarsinous acid by two routes: a) by the action of ethyldichloroarsine on glycols in presence of pyridine in a medium of absolute ether according to the scheme:

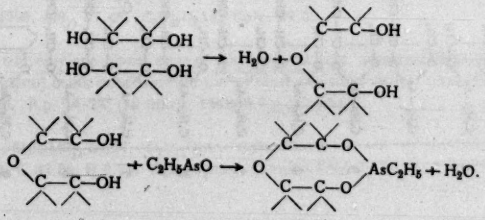


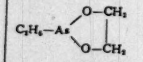
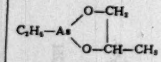
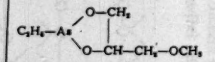
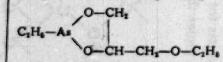
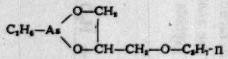
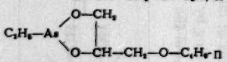
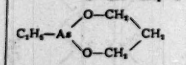
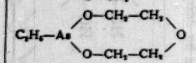
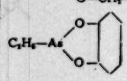
b) by interaction of ethylarsine oxide with the appropriate glycols at high temperature and in vacuum according to the scheme:



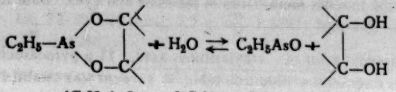
The second method gives the best results. We did not succeed in isolating the cyclic esters of ethylarsinous acid in the chemically pure form by the first method. These esters are always contaminated with a chlorine-containing product. The esters of ethylarsinous acid that we synthesized are listed in the table.

In their chemical properties, the cyclic esters of monoethylarsinous acid in many respects resemble the alkyl esters of cyclic glycolarsinous acids; with the exception of the crystalline pyrocatechylester, they are colorless, oily liquids with a sharp, specific odor. The ethylene glycol, propylene glycol, α-methoxypropylene glycol and α-n-propoxypropylene glycol esters of ethylarsinous acid (i.e. esters with lower boiling point) were not isolated in the chemically pure state, judging by the analysis for arsenic. We believe that the main impurities in these esters are formed by dehydration of the glycols under the influence of ethylarsine oxide according to the scheme:



No.	Formula of ester	Boiling point	d_4^{20}	n_D^{20}	MR_D	AR_D	% As found	% As calculated	% C found	% C calculated	% H found	% H calculated	Yield (%)
1		62° (10 mm)	1.5423	1.5230	32.49	9.64	43.8	45.67	28.18	29.29	5.77	5.53	78.5
2		52—53 (10 mm)	1.3859	1.4929	37.33	9.85	40.91	42.07	—	—	—	—	63.8
3		90 (10 mm)	1.3664	1.4880	43.87	10.13	32.33	36.01	—	—	—	—	79.5
4		99 (10 mm)	1.3167	1.4863	48.45	10.09	33.45	33.72	37.35	37.85	6.89	6.81	55.3
5		114 (11 mm)	1.2602	1.4818	53.39	10.42	29.54	31.72	—	—	—	—	74.3
6		124—125 (10 mm)	1.2402	1.4805	57.40	9.80	29.72	29.93	42.80	43.21	7.79	7.66	82.0
7		74—75 (10 mm)	1.4436	1.5212	37.57	10.09	41.44	42.07	33.35	33.72	6.21	6.22	57.5
8		90 (10 mm)	1.4070	1.5010	43.57	9.83	35.38	36.01	34.46	34.66	6.51	6.29	55.0
9		125 (13 mm)	M.p.	49—50°			35.70	35.32	—	—	—	—	—

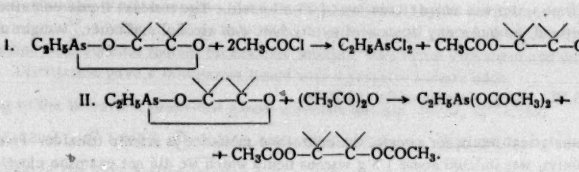
The cyclic esters of ethylarsinous acid are hydrolyzed in a more complex manner than the corresponding esters of arylarsinous acids. The following series of transformations evidently takes place, in this case, with separation of arsenic trioxide:



$$4C_2H_5AsO \longrightarrow [(C_2H_5)_2As]_2O + As_2O_3,$$
$$[(C_2H_5)_2As]_2O \longrightarrow (C_2H_5)_3As + C_2H_5AsO.$$

A similar transformation was observed by Valeur and Gailliot [3] in the oxidation of cacodyl oxide.

We studied the interaction of cyclic esters of ethylarsinous acid with acetyl chloride and acetic anhydride. In both cases double decomposition occurs according to the scheme:



I. $C_2H_5As(-O-C(-)-C(-)-O-) + 2CH_3COCl \longrightarrow C_2H_5AsCl_2 + CH_3COO-C(-)-C(-)-OCOCH_3.$

II. $C_2H_5As(-O-C(-)-C(-)-O-) + (CH_3CO)_2O \longrightarrow C_2H_5As(OCOCH_3)_2 +$

$+ CH_3COO-C(-)-C(-)-OCOCH_3.$

It is interesting to note that glycol esters of ethylarsinous acid react with methyl iodide. Thus, for example, the α-ethoxypropylene glycol ester of ethylarsinous acid enters into reaction with methyl iodide in the cold to form acicular crystals with a composition close to that of trimethylethylarsonium iodide.

EXPERIMENTAL

Preparation of the α-n-butoxypropylene glycol ester of ethylarsinous acid. 28.2 g hydroxyethylarsine was placed in an A. E. Arbuzov flask. A vacuum was then set up and the flask was heated on an oil bath to 90-100°. At this temperature 35 g of n-butoxypropylene glycol-1,2 was aspirated through the capillary tube in the course of 6 hours. The mixture was then heated to 130° for 3 hours. Fractionation gave the following fractions: 1st, 116-123° (10 mm), 1.3 g, n_D^{20} 1.4820; 2nd, 124-127° (10 mm), 54.3 g, n_D^{20} 1.4810; and a residue in the flask – a light-yellow liquid (3.8 g). Redistillation from a flask with a Widmer column gave 48.2 g of a fraction with b.p. 124-125° (10 mm).

Found %: As 29.72; C 42.80; H 7.79. $C_9H_{19}O_3As$. Calculated %: As 29.93; C 43.21; H 7.66.

The substance obtained – the α-n-butoxypropylene glycol ester of ethylarsinous acid – is a transparent, oily liquid with a characteristic, unpleasant odor.

d_4^{20} 1.2402, n_D^{20} 1.4805, MR_D 57.40. $C_9H_{19}O_3As$. Calc. 57.30.

Preparation of the trimethylene glycol ester of ethylarsinous acid. Reaction of 11.2 g ethylarsine oxide with 7.3 g trimethylene glycol, under conditions similar to those described above, gave the trimethylene glycol ester of ethylarsinous acid. B.p. 74-75° (10 mm). Yield 9.6 g (57.5%).

d_4^{20} 1.4436, n_D^{20} 1.5212, MR_D 37.57. $C_5H_{11}O_2As$. Calc. 37.19.
Found %: As 41.44; C 33.35; H 6.21. $C_5H_{11}O_2As$. Calculated %: As 42.07; C 33.72; H 6.22.

The ester is a transparent, oily liquid.

The other cyclic esters of ethylarsinous acid were prepared in similar fashion, starting from the corresponding glycols and ethylarsine oxide or ethyl dichloroarsine. The isolated cyclic esters of ethylarsinous acid, with the exception of the pyrocatechyl ester of ethylarsinous acid, are colorless, oily liquids. Many of them possess an unpleasant odor, irritating to the mucous membranes of the nose and eyes. Data for the synthesized esters are presented in the table.

Preparation of the pyrocatechyl ester of ethylarsinous acid. 11 g pyrocatechol and 11.9 g ethylarsine oxide were put into a distillation flask with a wide side tube. A vacuum was established in the system with the water jet pump, and the flask was heated gradually to 130° in the course of 5 hours. Distillation gave 18.3 g (86.5%) of a fraction with b.p. 124-125° (13 mm).

Found %: As 37.76, 35.58. $C_8H_9O_2As$. Calculated %: As 35.32.

The pyrocatechyl ester of ethylarsinous acid forms snow-white crystals with m.p. 49-50°.

Hydrolysis of the cyclic ester of ethylarsinous acid. 5.3 g of α-n-butoxypropylene glycol ester of ethylarsinous acid and 50 ml water were put in a porcelain dish and the mixture heated on a water bath. With progressive evaporation, fresh water was added (three lots of 20 ml each). The residual liquid contained white crystals which were filtered, washed many times with water, then with alcohol and ether. Weight after drying 1.3 g.

Found %: As 75.56. As_2O_3. Calculated %: As 75.74.

Judging by the analytical results for arsenic, the crystalline substance is arsenic trioxide. From the filtrate, after removal of the water, was isolated about 1.6 g viscous liquid which we did not examine closely. An attempt to obtain ethylarsinic acid by oxidation with 20% nitric acid solution of the cyclic ester of ethylarsinous acid was not successful. Instead of the expected product, we again isolated arsenic trioxide.

Action of methyl iodide on the α-ethoxypropylene glycol ester of ethylarsinous acid. To 5.7 g, α-ethoxypropylene glycol ester of ethylarsinous acid, was added 5 g methyl iodide. After several minutes at room temperature, fine acicular crystals began to separate out. The following day the crystals were filtered, washed three times with dry ether and dried in the air.

Found %: As 26.78; I 45.62. $C_5H_{14}IAs$. Calculated %: As 27.14; I 46.02.

The crystals are readily soluble in water and alcohol, insoluble in ether, benzene and gasoline. The substance that we isolated is probably impure trimethylethylarsonium iodide.

Action of acetyl chloride on the α-n-butoxypropylene glycol ester of ethylarsinous acid. 12.1 g α-n-butoxypropylene glycol ester of ethylarsinous acid was put in a distillation flask, and 8.2 g acetyl chloride was added from a dropping funnel; during the addition the temperature of the reaction mixture rose sharply from 24 to 100°. The flask was then heated to 170° for one hour. The next day the mixture was distilled in vacuum to give the following fractions: 1st, 70-90° (118 mm), n_D^{20} 1.5355, 7.2 g; 2nd, 126-134° (11 mm), n_D^{20} 1.4262, 9.5 g. Redistillation of the 1st fraction gave 5.1 g substance with b.p. 96° (105 mm), n_D^{20} 1.5495.

Found %: As 42.15; Cl 41.02. $C_2H_5Cl_2As$. Calculated %: As 42.81; Cl 40.57.

According to the literature [4], ethyldichloroarsine has b.p. 90° (100 mm), $n_D^{14.5}$ 1.5588.

From the second fraction was isolated 7.3 g substance with b.p. 133.5° (11 mm).

Found %: C 56.29, 56.34; H 8.67, 8.58. $C_{11}H_{20}O_5$. Calculated %: C 56.88; H 8.68.

The analytical data indicate that the substance is α-n-butoxypropylene glycol diacetate.

d_4^{20} 1.0272, n_D^{20} 1.4263, MR_D 57.98. $C_{11}H_{20}O_5$. Calc. 57.75.

Reaction of acetyl chloride with the α-n-butoxypropylene glycol ester of ethylarsinous acid consequently involves an exchange reaction with formation of ethyldichloroarsine and α-n-butoxypropylene glycol diacetate.

Action of acetyl chloride on the α-n-propoxypropylene glycol ester of ethylarsinous acid. Mixing of 9.6 g of the α-n-propoxypropylene glycol ester of ethylarsinous acid with 6.2 g acetyl chloride caused a temperature rise from 20 to 145°. The flask was heated on an oil bath to 160° for 30 minutes. Vacuum distillation gave the following fractions: 1st, 72-83° (70 mm), 7.7 g, n_D^{20} 1.5521; 2nd, 115-123° (13 mm), 1.2 g, n_D^{20} 1.4311; 3rd, 124-127° (13 mm), 6.7 g, n_D^{20} 1.4258.

Redistillation of the 1st fraction gave 5.1 g ethyldichloroarsine with b.p. 80-81° (64 mm), n_D^{20} 1.5580.

Found %: As 42.85; Cl 40.23. $C_2H_5Cl_2As$. Calculated %: As 42.81; Cl 40.67.

The 3rd fraction yielded 4.2 g α-n-propoxypropylene glycol diacetate.

B.p. 123-124° (12 mm), d_4^{20} 1.0440, n_D^{20} 1.4256, MR_D 53.52. $C_{10}H_{18}O_5$. Calc. 53.13.

Action of acetic anhydride on the propylene glycol ester of ethylarsinous acid. A mixture of 10.4 g propylene glycol ester of ethylarsinous acid and 11.9 g acetic anhydride in a distillation flask was heated at 180-200° for 12 hours. Vacuum distillation gave the following fractions: 1st, 30-55° (11 mm), n_D^{18} 1.3862, 3.9 g; 2nd, 55-97° (11 mm), n_D^{18} 1.4214, 10.75 g; 3rd, 98-140° (with decomp., 11 mm), n_D^{18} 1.4620, 4.2 g. The 2nd fraction was washed with aqueous sodium bicarbonate solution, then twice with water and dried over calcined sodium sulfate. Distillation gave a transparent liquid with a pleasant acetate odor.

According to the literature, propylene glycol diacetate has b.p. 190.2°, d_4^{20} 1.059.

B.p. 188.5-189.5°, d_4^{20} 1.0572, n_D^{20} 1.4118, MR_D 37.68. $C_7H_{12}O_4$. Calc. 37.68.

Redistillation of the high-boiling fraction gave a substance with b.p. 126-127° (10 mm).

Found %: As 33.15. $C_2H_5As(OCOCH_3)_2$. Calculated %: As 33.73.

The substance is evidently diacetoxy-ethylarsine.

d_4^{20} 1.3300, n_D^{20} 1.4690, MR_D 46.50. $C_6H_{11}O_4As$. Calc. 46.87.

Action of acetic anhydride on α-n-butoxypropylene glycol ester of ethylarsinous acid. A mixture of 12.6 g of the α-n-butoxypropylene glycol ester of ethylarsinous acid, and 11.0 g acetic anhydride was heated in a sealed tube for 3 hours at 200° and for 1 hour at 240°. Considerable pressure was released when the tube was opened. The gases had a sharp odor reminiscent of cacodyl. Suitable working up of the dark-brown liquid led to separation of α-n-butoxypropylene glycol diacetate in the pure form.

B.p. 133.5° (11 mm), d_4^{20} 1.0241, n_D^{20} 1.4265.

No other individual substances could be isolated.

SUMMARY

1. Some representatives of cyclic esters of ethylarsinous acid were synthesized and studied.

2. Hydrolysis of these esters is found to go in a complex manner with formation of arsenic trioxide instead of the expected ethylarsine oxide.

3. Esters of ethylarsinous acid are found to enter into a double decomposition reaction with acetyl chloride and acetic anhydride.

4. Methyl iodide reacts in the cold with the glycol ester of ethylarsinous acid to form white crystals, which are probably trimethylethylarsonium iodide.

LITERATURE CITED

[1] Ya. F. Komissarov et al., Proc. Acad. Sci. USSR 55, 428 (1947).

[2] Gilm Kamai and N. A. Chadaeva, Proc. Acad. Sci. USSR 86, 71 (1952); J. Gen. Chem. 23, 1431 (1953) (T.p. 1499)*; G. Kamai et al., Proc. Acad. Sci. USSR 89, 1015 (1953).

[3] A. Valeur and P. Gailliot, Chem. Zentr. 1927, II, 1014.

[4] C. S. Gibson and J. D. A. Jahnson, J. Chem. Soc. 1931, 2518; E. Gryszkiewiez-Trochimowski and S. F. Sikorski, Bull. Soc. Chim. (4), 41, 1570 (1927).

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* T.p. = C. B. Translation pagination.

THE REACTION OF TRIPHENYLFLUOROSILANE AND OF TRIPHENYLCHLOROMETHANE WITH DIPHENYLAMINE IN PRESENCE OF LITHIUM

V. S. Chugunov

Organosilicon compounds containing, directly at the silicon atom, an amino group, both of whose hydrogens are substituted by phenyl radicals, have not been known up to now. The attempts of Reynolds [1] to link diphenylamine to a silicon atom were unsuccessful. Starting from triphenylfluorosilane and diphenylamine and with participation of lithium, we have realized the synthesis of triphenyl-(diphenylamino)-silane according to the equation

$$(C_6H_5)_3SiF + (C_6H_5)_2NH \xrightarrow{Li} (C_6H_5)_3SiN(C_6H_5)_2.$$

Under analogous conditions, triphenylchloromethane reacts with diphenylamine with formation of triphenyl-(diphenylamino)-methane.

Triphenyl-(diphenylamino)-silane easily hydrolyzes when boiled in alcohol acidified with hydrochloric acid, and forms triphenylsilanol and diphenylamine, whereas triphenyl-(diphenylamino)-methane remains unchanged under these conditions.

In contrast to the behavior of arylhalosilanes, alkylchlorosilanes react with diphenylamine even in the cold, and they form complex compounds similar to the previously prepared $(C_6H_5)_2NH \cdot SiF_4$ [2]. For example, tri-n-butylchlorosilane and diphenylamine form the crystalline $(p\text{-}C_4H_9)_3SiCl \cdot HN(C_6H_5)_2$; under these conditions, di-n-butyldichlorosilane gives $(p\text{-}C_4H_9)_2SiCl_2 \cdot 2HN(C_6H_5)_2$.

EXPERIMENTAL

Triphenyl-(diphenylamino)-silane. 11.2 g triphenylfluorosilane in 50 ml toluene, 7.5 g diphenylamine and 1.4 g lithium were placed in a flask with a tube; a reflux condenser was also attached. The contents were boiled for 6 hours with continuous passage of a stream of hydrogen, which had been dried over concentrated sulfuric acid and potassium hydroxide. The excess of unreacted lithium and the lithium fluoride were then filtered off. From the filtrate was obtained 5.4 g crystals (yield 20% , reckoned on the triphenylfluorosilane) of triphenyl-(diphenylamino)-silane in the form of an equimolar compound with toluene. The toluene was eliminated by heating the compound (2.51 g) in vacuum. Yield 2.06 g triphenyl-(diphenylamino)-silane with m.p. 224-225°, practically insoluble in alcohol and ether.

Found %: Si 6.4; N 3.2. M 416. $C_{30}H_{25}NSi$. Calculated %: Si 6.6; N 3.3. M 427.

Triphenyl-(diphenylamino)-methane. Preparation was effected under similar conditions, starting from 14 g triphenylchloromethane in 50 ml toluene, 9 g diphenylamine and 1.4 g lithium. Triphenyl-(diphenylamino)-methane was obtained (in 45% yield reckoned on the triphenylchloromethane) with m.p. 249-250° (from toluene).

Found %:* C 90.30; H 6.12; N 3.3. $C_{31}H_{25}NSi$. Calculated : C 90.47; H 6.12; N 3.4.

* Determinations of C and H were made by Yu. N. Platonov, to whom we express our thanks.

Hydrolysis of triphenyl-(diphenylamino)-silane. To 0.5 g triphenyl-(diphenylamino)-silane was added 30 ml of 90% ethyl alcohol, acidified with 1 ml concentrated hydrochloric acid, and the mixture was boiled for an hour. Dilution of the alcoholic solution with water gave 0.3 g triphenylsilanol [3] with m.p. 153° (from toluene). The substance was recovered unchanged when 0.5 g triphenyl-(diphenylamino)-methane was boiled under the same conditions.

Organosilicon complex compounds. Copious separation of a complex occurs on adding 10 g diphenylamine in 50 ml toluene to 10.8 g tri-n-butylchlorosilane, even at room temperature. Recrystallization from toluene gave 18.4 g $(p\text{-}C_4H_9)_3SiCl \cdot HN(C_6H_5)_2$ with m.p. 172-175° (decomp.).

From 5.4 g di-n-butyldichlorosilane and 10.6 g diphenylamine in 30 ml toluene was obtained 12 g $(p\text{-}C_4H_9)_2SiCl_2 \cdot 2HN(C_6H_5)_2$ with m.p. 160-164° (decomp.).

The compounds are unstable; they decompose when kept in a sealed ampoule and turn light green.

Formula	Found		Calc.	
	Si	Cl	Si	Cl
$(p\text{-}C_4H_9)_3SiCl \cdot HN(C_6H_5)_2$	6.4	8.8	6.9	8.7
$(p\text{-}C_4H_9)_2SiCl_2 \cdot 2HN(C_6H_5)_2$	4.8	13.1	5.1	12.8

SUMMARY

1. By means of an organolithium synthesis, the preparation was effected for the first time of triphenyl-(diphenylamino)-silane and triphenyl-(diphenylamino)-methane.

2. Unlike triphenylfluorosilane, tri-n-butylchlorosilane and di-n-butyldichlorosilane react with facility with diphenylamine, with formation of the corresponding organosilicon complex compounds.

LITERATURE CITED

[1] H. H. Reynolds, Chem. News 65, 214 (1892).

[2] A. M. Comey and C. L. Jackson, Am. Chem. J. 10, 174 (1888).

[3] N. S. Nametkin et al., Proc. Acad. Sci. USSR 83, 705 (1952).

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THE ROLE OF OXIDATION-REDUCTION SYSTEMS IN THE PROCESS OF VULCANIZATION WITH SULFUR

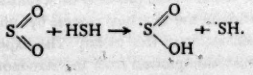
E. I. Tinyakova, E. K. Khrennikova, B. A. Dolgoplosk, V. N. Reich and T. G. Zhuravleva

Although numerous studies have been made of sulfur vulcanization, its mechanism still remains obscure. This is particularly true of the role of accelerators of vulcanization and of the mechanism of formation of mono- and polysulfide bonds in vulcanizates.

In the present communication we attempt to approach the process of sulfur vulcanization from the standpoint of a possible role of oxidation-reduction systems as a source of free radicals. This approach is justified by our earlier investigations, in which we established the possibility of applying oxidation-reduction systems to the building-up and breakdown of polymers in hydrocarbon media [1].

The mechanism of the Peachey vulcanization process. The feasibility of the Peachey process is usually regarded as evidence of the role of active sulfur in the vulcanization process. As we know, the Peachey process involves alternate treatment of rubber at room temperature with gaseous SO_2 and H_2S [2]. According to the generally accepted theory, the reaction between H_2S and SO_2 in a rubber medium leads to formation of free sulfur, which in the nascent form brings about vulcanization at room temperature.

As in many other oxidation-reduction reactions of this type, the mechanism of the process can only be correctly understood by considering its intermediate bimolecular stages. We assumed that the vulcanizing action of a system consisting of SO_2 and H_2S is associated not with the release of "active" sulfur, but with intermediate reaction stages, for example:



Attempts to isolate these intermediate products with the help of triphenylmethyl (by introducing hexaphenylethane into the system) were, however, unsuccessful.

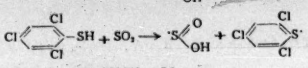
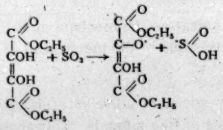
$$(C_6H_5)_3C^{\cdot} + {}^{\cdot}SH \longrightarrow (C_6H_5)_3CSH,$$
$$(C_6H_5)_3C^{\cdot} + {}^{\cdot}SO_2H \longrightarrow (C_6H_5)_3CSO_2H.$$

Neither mercaptan nor sulfinic acid could be detected in appreciable amounts in the reaction products after filtering from the separated sulfur. The process goes smoothly in the direction of separation of free sulfur.

With the objective of conducting the reaction under conditions excluding the possibility of separation of free sulfur, we replaced hydrogen sulfide by trichlorothiophenol and other reducing agents. The action of these compounds was studied in a xylene solution of butadiene rubber, and was characterized by the period of formation of a gel.

TABLE 1

Vulcanization of Rubber in Xylene Solution

Preparation	Proposed reactions	Temperature	Time required for gelling
1	a) $2H_2S + SO_2 \longrightarrow 2H_2O + 3S$ b) $H_2S + SO_2 \longrightarrow HS\cdot + \cdot S\!\!\overset{O}{\underset{OH}{<}}$	20°	Instantaneous
2		0	Instantaneous
3	$HSCH_2CH_2OCH_2CH_2SH + SO_2 \longrightarrow$ $\longrightarrow HSCH_2CH_2OCH_2CH_2S\cdot + \cdot S\!\!\overset{O}{\underset{OH}{<}}$	100	After 1 hour
4		100	After 15 minutes

As we see from the data presented in Table 1, a gel is even formed at 0° in presence of trichlorothiophenol and SO_2; a gel is formed at a higher temperature in presence of diethyl dihydroxymaleate and SO_2 or of β,β'-dimercaptodiethyl ether and SO_2. In all these cases, the reaction goes without separation of free sulfur. Gelation does not occur on treatment with sulfur dioxide in the absence of mercaptan or ester of dihydroxymaleic acid under the above conditions. Sulfur and chlorine were determined, after numerous washings with ethyl alcohol, in the gel obtained with the help of trichlorothiophenol and SO_2. Found %: S 3.81; Cl 4.03, corresponding to 8.1% of combined trichlorothiophenol and 5.2% SO_2. These results show that the reaction is accompanied by the addition of reactants to an unsaturated polymer chain, reminiscent of the addition of mercaptans and SO_2 under the influence of peroxides and other substances forming free radicals.

The implication of these facts is that the reaction between trichlorothiophenol and SO_2 goes with formation of free radicals, which have the same effect as the products of breakdown of peroxides. Most significant is the fact that replacement of hydrogen sulfide in the Peachey process by other reducing agents leads to development of a vulcanization process without separation of free sulfur. The experimental material enables us to regard the mechanism of the Peachey vulcanization process from the standpoint not of initiation by nascent sulfur, but of initiation by intermediate reaction products.

Reaction of sulfur with vulcanization accelerators as an oxidation-reduction process. Our earlier studies had established that the reaction between oxygen and a series of reducing agents, many of which are accelerators of vulcanization with sulfur, initiates the process of oxidative breakdown of rubbers in presence of very small amounts of iron salts (soluble in hydrocarbons) [1].

In many chemical reactions, sulfur behaves like oxygen, but with the important difference that the end product of reaction is an extremely reactive substance – hydrogen sulfide. The latter adds on at the double bond in presence of free radicals. A number of investigators observed the formation of hydrogen sulfide during the vulcanization process. Fischer and other investigators pay great heed to the possible role of H_2S in the vulcanization process [3].

In the present investigation we have shown that many vulcanization accelerators react with sulfur with formation of considerable amounts of hydrogen sulfide (Table 2). In some cases this process goes with appreciable speed, even at temperatures below 100°.

The data of Table 2 show that the reaction of sulfur with various reducing agents leads to formation of hydrogen sulfide. The latter is formed in high yield in reactions with phenylhydrazine and hydrazobenzene

TABLE 2

Formation of Hydrogen Sulfide in the Reaction of Various Reducing Agents with Sulfur in Xylene Solution

Reducing agent	Temperature	Duration of reaction (in hours)	Yield of H_2S (%)		Reducing agent	Temperature	Duration of reaction (in hours)	Yield of H_2S (%)	
			argentometrically	iodometrically				argentometrically	iodometrically
Without reducing agent	143+ 160	5	0	—		80	1		12.4
						143	0.25	25.0	14.2
Phenylhydrazine	143	5	68.0	—		143	0.5	35.0	20.0
Hydrazobenzene	143	5	34.0	—	Monoethanolamine	143	0.91	38.8	28.2
						143	3	40.9	—
Cyclohexene	143	5	4.0	—		143	5	49.0	—
Dihydronaphthalene	143	5	10.8	—		143	7	74.0	—
Glycolic aldehyde*	143	1	—	8		143	9	97.7	—
	143	2	—	17		80	1	—	30.0
	143	4	—	23	Ethylenediamine	143	0.25	51.0	24.6
Glycerol*	160	5	—	29		143	0.5	51.7	23.6
Glucose*	160	5	—	40		143	1	54.9	28.1
	80	1	—	20.2	Tetraethylenediamine				
	143	0.5	21.6	16.7		143	5	—	52.0
Polyethylene polyamines	143	1	31.2	20.5					
	143	3	33.2	—					
	143	5	43.2	—					

* The solvent was a mixture of 30% pyridine and 70% xylene (by volume).

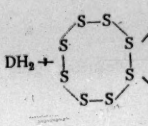
which, in hydrocarbon solution, as we showed earlier, are oxidized by atmospheric oxygen at room temperature with very great facility with formation of hydrogen peroxide [1]. Hydrogen sulfide is formed in small quantity in the reaction with cyclohexene, which typifies the structure of polybutadiene (1-4 links). In this case, the yield of hydrogen sulfide is very low because the reaction goes further with formation of mercaptan and monosulfide. As reducing agents in the reaction with sulfur, we also tried other substances which had not previously been tested or applied as vulcanization accelerators (ethanolamines, ethylenediamine and some of its derivatives, glucose, fructose and benzoin). The most active reducing agents are monoethanolamine and ethylenediamine with which the reaction goes, even at 80°. It should be noted that the yield of hydrogen sulfide by the argentometric method is higher than by the iodometric method. The reasons for this discrepancy will be discussed below.

It is extremely interesting that tetraethylenediamine is also an active donor of hydrogen in reaction with sulfur (the yield of hydrogen sulfide reaches 52%), which points to the absence of a direct link between the presence of NH groups and reducing properties in the reaction under consideration. All these compounds exert an accelerating action on the process of vulcanization with sulfur. Ethylenediamine and its derivatives are vulcanization accelerators at 100-140°; benzoin, glucose, fructose and glycerol are active at 160°.

A characteristic feature of these vulcanization accelerators is the increased stability of the unfilled rubbers. For example, unfilled rubbers from SKS 30-A rubber, obtained by using benzoin, glucose or fructose, have a tensile strength of about 130 kg/cm^2 with a relative elongation of 850% and a permanent deformation of 24%. The same rubbers, obtained with the help of ethylenediamine and ethanolamines, have a tensile strength of up to 200 kg/cm^2. It is highly probable that the formation of hydrogen sulfide in these cases goes through the intermediate steps of unstable compounds whose breakdown may lead to formation of the primary radical $^{\cdot}SH$.

According to modern ideas, the molecule of sulfur is a ring of 8 atoms; the mean energy of the bond between them (according to thermodynamic data) is 64 kcal. According to Zapp's theory [4], the sulfur ring is

made up of four S_2 segments; the energy of the bonds between each of these segments is only 32 kcal, whereas the S–S bond energy inside a segment is nearly 102 kcal. On this basis, the reaction of sulfur with reducing agents may go either in the direction of rupture of the ring at each S – S bond, or with cleavage of a segment of two sulfur atoms:



(1)

(2)

Breakdown of the 8-membered ring must lead, in the initial stage, to formation of the extremely unstable hydrogen persulfide. It is known [10] that hydrogen persulfide, the analog of hydrogen peroxide, easily breaks down to form hydrogen sulfide and free sulfur: $H_2S_2 \rightarrow H_2S + S$. The intermediate steps of this reaction can, by analogy with hydrogen peroxide, be associated with formation of $^{\cdot}SH$ radicals: $H_2S_2 \rightarrow 2\ ^{\cdot}SH$. The radical character of the intermediate steps of the reaction is confirmed by our data on structure formation in rubber with hydrogen persulfide, and by the exchange reaction between hydrogen persulfide and sulfur-labeled hydrogen sulfide (H_2S^{35}).

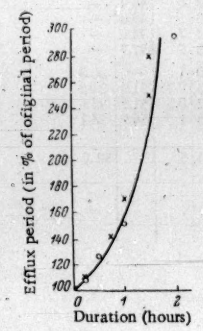


Fig. 1. Change of viscosity of a rubber solution in ethyl benzene in presence of H_2S_2 at 50°.

The change of viscosity of a 4% solution of butadiene-styrene rubber in presence of hydrogen persulfide in the proportion of 5% of the rubber at 50°,* is plotted in Fig. 1. Experiments were carried out in glass ampoules. The viscometers have been described previously [1].

After 4 hours, the whole of the solution had changed into gel. At 70° the gel is formed in 1 hour 40 minutes, at 100° in 20 minutes. In the absence of hydrogen persulfide, the viscosity does not alter.

We studied the kinetics of decomposition of hydrogen persulfide in ethylbenzene solution at 50 and 70°.

The velocity of the process was characterized by the amount of hydrogen sulfide formed and taken up by 10% cadmium chloride solution.

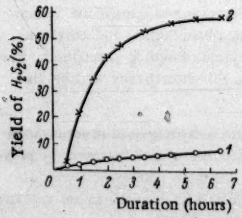


Fig. 2. Decomposition of H_2S_2 in ethylbenzene solution at 70°.
1) Quartz ampoule; 2) glass ampoule.

Owing to the great sensitivity of hydrogen persulfide to caustic alkali (even traces from glass), experiments were run in quartz ampoules fitted with a tube extending to the bottom. A continuous stream of dry nitrogen was passed through this tube throughout the experiment (to remove hydrogen sulfide from the solution). The experimental data are plotted in Fig. 2. Thermal decomposition of hydrogen persulfide at 70° goes at an insignificant velocity (Curve 1). In an ampoule of ordinary glass hydrogen persulfide breaks down very quickly (Curve 2).

* Hydrogen persulfide was prepared by fractional distillation in vacuum [19] of hydrogen monosulfide (b.p. 75°, 760 mm), and was kept in an atmosphere of dry hydrogen chloride at –70°.

Vulcanization under the influence of hydrogen sulfide and mercaptans.* The addition of hydrogen sulfide and mercaptans to unsaturated compounds in presence of oxygen or peroxides has been amply studied and well clarified in the literature [5,6]. Other studies have been made of the addition of hydrogen sulfide and mercaptans to rubber, and have also shown that the reaction goes under the influence of oxygen or peroxides [7,8].

We established that structure formation in butadiene rubber by hydrogen sulfide or dimercaptan goes under the influence of any free radicals obtained by breakdown of various peroxides and azo and diazo compounds. Experiments were carried out with a solution of butadiene rubber (containing about 50% of 1-4 links in the chain). The compound selected for study of the vulcanizing action of dimercaptans was β,β'-dimercaptodiethyl ether ($HSCH_2CH_2-OCH_2CH_2SH$). Addition of hydrogen sulfide or dimercaptan to double bonds leads to structure formation in the polymers, and to formation of a gel (Table 3). In the absence of dimercaptan and

TABLE 3

Structuring of Rubber in Solution by Dimercaptan and Hydrogen Sulfide in Presence of Free Radicals **

Initiator-source of free radicals	Radicals (initial active centers)	Concentration of initiator M · 10²	Temperature	Period for development of gel in presence of (in min.)	
				dimercaptan	H_2S
Methyl-phenyltriazene $CH_3N=NNHC_6H_5$	$CH_3^{\cdot}$	1.48	100°	5	10
Diazoaminobenzene $C_6H_5N=NNHC_6H_5$	$C_6H_5^{\cdot}$	1.0	100	20	60
Azobutyric acid dinitrile $(CH_3)_2C(CN)-N=N-C(CN)(CH_3)_2$	$CH_3-CH_2-C^{\cdot}(CH_3)(CN)$	1.20	80	5	20
Benzoyl peroxide $C_6H_5CO-O-O-CO-C_6H_5$	$C_6H_5COO^{\cdot}$ and $RS^{\cdot}$ ($^{\cdot}SH$)	1.24	20	Starts immediately after mixing of components	
Isopropylbenzene hydroperoxide $C_6H_5C(CH_3)_2-OOH$	$C_6H_5C(CH_3)_2-O^{\cdot}$ $RS^{\cdot}$ ($^{\cdot}HS^{\cdot}$)	1.80	20	Starts immediately after mixing of components	

hydrogen sulfide, all the substances mentioned do not bring about a vulcanizing action under corresponding conditions. The vulcanizing action of benzoyl peroxide and isopropylbenzene hydroperoxide at 20° is caused by the development of oxidation-reduction reactions of a radical type:

$$ROOH + R'SH(HSH) \longrightarrow RO^{\cdot} + H_2O - R'S^{\cdot}(HS^{\cdot}).$$

Diazo compounds (methyl-phenyltriazene and diazoaminobenzene) and azo-iso-butyric acid dinitrile have a gelation effect at higher temperatures corresponding to the temperature of their thermal breakdown.

The problem of the role of accelerators in the process of vulcanization with sulfur. Up to recent times, the action of accelerators in the process of vulcanization with sulfur has usually been regarded as a catalytic action. The following scheme has been advanced in explanation of the effect [9]:

$$\text{Accel.} + S \rightarrow (\text{Accel.} \ldots S) \rightarrow \text{Accel.} + S^{***}$$

* This section of the work was carried out with collaboration of M. P. Tikhomolova.

** The concentration of rubber in solution was 5%, that of β,β'-dimercaptodiethyl ether was $2.2 \cdot 10^{-2}$ M.

*** Active sulfur.

This theory assumes the initial formation of a complex (Accel.... S) which subsequently breaks down with regeneration of the accelerator and separation of sulfur in an active form. Addition of the latter by some mechanism or another is accompanied by a vulcanizing effect.

B. A. Dogadkin [9] suggests that vulcanization can also go without the step of separation of active sulfur as a result of direct reaction of the rubber with the complex:

$$(\text{Accel.}\ldots\text{S}) + \text{rubber} \rightarrow \text{vulcanizate} + \text{Accel}$$

In this case again, the accelerator functions as a catalyst of the process.

We shall now consider the various types of known organic vulcanization accelerators in the light of the possible participation of radical reactions.

The 1st group of vulcanization accelerators are substances capable of thermal breakdown to free radicals, for example, thiurams and compounds of the type of dibenzothiazole disulfide, the structure of which is similar to that of acyl peroxides. Compounds of this type can break down to free radicals at temperatures of 100° and higher [10]. They easily add on to double bonds to give a polymerizing effect or they split off hydrogen from the rubber or solvent with transition to the corresponding thiols. This group of accelerators of vulcanization with sulfur should evidently also include accelerators of the type of polysulfides, as well as sulfenamide accelerators, containing an unstable S–N bond, such as benzothiazole-2-sulfendiethylamide (Vulcacit A-Cet). Compounds of this type, as we know from experience with diazothio compounds, are capable of initiating the process of polymerization in emulsions, even in a homogeneous medium [11]. The known ability of "Altax" and sulfenamide accelerators to dissociate into free radicals enabled B. A. Dogadkin to regard vulcanization under the influence of such compounds in the absence of sulfur as a process akin to polymerization [12].

Representatives of the 2nd group of vulcanization accelerators are mercaptans, dithiocarbamates and their amine salts, various primary, secondary and tertiary amines (ethylenediamine and its alkyl derivatives, ethanolamines, guanidines), products of condensation of amines with aldehydes, p-phenylenediamine, etc., hydroxyaldehydes, hydroxyketones such as glucose, fructose and benzoin, and polyhydric alcohols. We established the accelerating effect of hydroxycarbonyl compounds upon the process of vulcanization with sulfur with reference to rubbers of various types.

In our opinion, the mechanism of the action of the 2nd group of accelerators of sulfur vulcanization (mercaptans, amines and hydroxycarbonyl compounds) can be explained on the basis of the known role of such compounds in various oxidation-reduction systems used for the initiation of radical processes. All these compounds are characterized by reducing properties and by the ability, under specific conditions, to quickly react with peroxides or oxygen with manifestation of polymerizing or structuring effects and of oxidative destruction of polymers [1, 14, 15, 16]. The following scheme illustrates the general role of the systems with participation of peroxides: $DH_2 + ROOH \rightarrow DH + H_2O + RO^{\cdot}$, where DH_2 is a reducing agent. Reactions of this type, accompanied by separation of water or other products, are energetically more favored than direct thermal breakdown of peroxides, and they proceed at lower temperatures.

It was shown above that many representatives of the 2nd group of accelerators react with sulfur at temperatures considerably below the temperature of thermal breakdown of S_8, and form considerable amounts of hydrogen sulfide. Some of them, for example ethylenediamine and ethanolamines, reduce sulfur to hydrogen sulfide, even at 50-70° and bring about a structuring effect under suitable conditions. The following scheme may be advanced to account for the action of many accelerators of sulfur vulcanization which react with sulfur with formation of hydrogen sulfide:

$$DH_2 + S_8 \xrightarrow{1} D + H_2S_2 \rightarrow {}^{\cdot}SH \rightarrow H_2S.$$
$$DH_2 + S_8 \xrightarrow{2} D + HS_8H \rightarrow {}^{\cdot}SH \rightarrow H_2S.$$

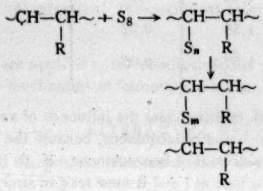
Initiation of the process of vulcanization is evidently bound up, just as in oxygen systems, with the intermediate stages of the reaction. This view is supported by our observation that hydrogen persulfide causes vulcanization of a polymer on decomposing in hydrocarbon solution. In the absence of vulcanization accelerators, the

role of reducing agent is played by the polymeric chain itself, as is confirmed by the formation of hydrogen sulfide, mercaptans and sulfides on reaction of cyclohexene or other unsaturated hydrocarbons with sulfur at a temperature of about 140°. This reaction evidently proceeds at the expense of the C–H bond in groups located in the α-position to the double bond. The poor efficiency of the process of sulfur vulcanization in the absence of accelerators is due to the low velocity of reaction of the polymer chain with sulfur. Hydroxycarbonyl compounds, ethylenediamine, ethanolamines and mercaptans react with sulfur at lower temperatures, and thus accelerate the process as a whole. Consequently, the primary initiation of the vulcanization process is due either to thermal breakdown of the initiator (1st group of accelerators), or to the oxidation-reduction reaction between vulcanization accelerators and sulfur, which leads to formation of ·SH radicals.

Our earlier studies [13] on free-radical reactions with sulfur in model systems gave an insight into the mechanism of formation of mono- and polysulfide bonds in vulcanizates when the process was initiated by free radicals. Two courses are possible during vulcanization:

$$1)\quad R^{\cdot} + S_8 \longrightarrow RS_nR,$$
$$2)\quad R^{\cdot} + R_1SH(H_2S) \longrightarrow RH + R_1S^{\cdot}(HS^{\cdot}).$$

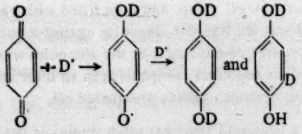
In the absence of mercaptans and hydrogen sulfide, the reaction goes mainly by the first route, leading to formation of polysulfide bonds:



In presence of hydrogen sulfide and mercaptans, the reaction goes mainly by the second route with formation of monosulfide bonds. A chain mechanism of addition of hydrogen sulfide or mercaptans to olefins has been examined by Kharasch and other investigators [17].

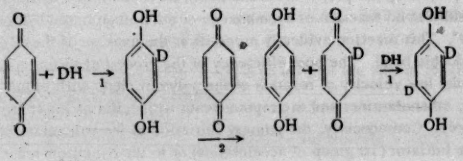
Our experimental results show that there is little formation of polysulfide bonds when using vulcanization accelerators that react with sulfur with liberation of a considerable amount of hydrogen sulfide (Table 4).

It appears to us that the mechanism of vulcanizing action of nitro compounds and quinones can be approached on the basis of their behavior in reactions with free radicals and reducing agents. The inhibiting effect of benzoquinone in radical processes is governed by the following reactions [10]:



(I)

In reactions with reducing agents, benzoquinone passes into the corresponding derivatives of hydroquinone:



(II)

TABLE 4

Content of Polysulfide Sulfur in Vulcanizates of SKS-30A Rubber in Presence of Monoethanolamine and Ethylenediamine

Accelerator	Sulfur content (%)		Relative amount of polysulfide sulfur (in % of total)
	total combined	polysulfide	
Diphenylguanidine	1.41	0.20	14.18
Monoethanolamine	1.59	0.02	1.26
Ethylenediamine	1.57	0.03	1.91

Reaction (I), as we know, proceeds with facility under the influence of various reducing agents. Reaction (II) also goes easily between alkylhydroquinone and benzoquinone, because the oxidation-reduction potential of alkylquinones is appreciably lower than the potential of benzoquinone. If D is a polymeric free radical and DH is a polymer chain, then reactions of the type of I and II must lead to structure-formation in the chain. Aromatic nitro compounds are inhibitors of radical processes, and the intensity of the effect increases with increasing number of nitro groups [10]. The intensity of the vulcanizing effect also increases in the same order [18].

Aromatic nitro compounds belong to the type of quinoid inhibitors of radical processes because of the two types of reactions leading to inhibition $R^{\cdot} + AH \rightarrow RH + A^{\cdot}$ and $R^{\cdot} + AH \rightarrow RAH$ (where $A^{\cdot}$ and RAH are considerably less active than $R^{\cdot}$), only the second mechanism of the quinoid type is realized with nitro compounds. This was demonstrated by the quantitative capture of a methyl radical by trinitrobenzene without formation of methane [10]. Consequently, what has been said about a possible mechanism of the vulcanizing action of quinones is also applicable to polynitro compounds.

Experimental Procedure and Analytical Methods

a) Experiments on the vulcanizing action of systems with participation of SO_2 were performed with 5% solution of butadiene rubber, stabilized with phenyl-β-naphthylamine. Ampoules were filled in absence of oxygen. The ampoules were evacuated with an oil pump, and then filled with gaseous SO_2, following which the solution of rubber with reducing agent was fed into the ampoules against a back-pressure of SO_2; the ampoules were then sealed off. In the case of systems containing H_2S, the ampoules were pumped out, filled with inert gas, and charged with a solution of rubber and other components in an inert atmosphere; the ampoules were then cooled, rapidly pumped out, filled with hydrogen sulfide and sealed off.

The ampoules were charged in a stream of inert gas when studies of the vulcanizing action of dimercaptans, in presence of various inhibitors, were being undertaken.

b) Study of the reaction of sulfur with various compounds. The reaction was studied in xylene solution, and sometimes in a xylene-pyridine mixture in the ratio of 70:30 by volume at temperatures of 80-160°. The sulfur content of the solution was 1 wt.-%, and the substances under test were taken in equimolar amounts in relation to sulfur. Experiments were carried out in sealed ampoules. After completion of the heating, the ampoules were cooled to −70° and opened. The amount of H_2S formed was determined by the argentometric method [20], or by the iodometric method [21]. In the first case a definite volume of reaction mixture was put into a flask (ground-glass stopper), containing 0.05 N $AgNO_3$ solution, the mixture was shaken 1 minute, and the excess of $AgNO_3$ was

titrated with 0.05 N ammonium thiocyanate solution. In the second case, a nitrogen stream was passed through the reaction mixture (at first with cooling and later with heating) for complete removal of dissolved hydrogen sulfide. The latter was absorbed by cadmium chloride solution. At the end of the reaction, a definite volume of 0.1 N iodide-iodate solution and HCl was run into the CdS suspension. The iodine that did not enter into reaction was titrated with 0.05 N hyposulfite solution.

It should be mentioned that the argentometric method of determination of hydrogen sulfide in the products of reaction of sulfur with amines gives higher results than the iodometric method. It may be assumed that the first step in the reaction of sulfur with amines which, in some cases, goes even at room temperature, is the formation of a complex in which the hydrogen of the amino compound is already partly in the ionized state. On addition of silver nitrate solution, a precipitate of silver sulfide is immediately formed. The iodometric method (with cadmium salts) is based on the determination of only the evolved hydrogen sulfide.

SUMMARY

1. The reaction between trichlorothiophenol or dienols and SO_2 brings about vulcanization of rubber with separation of elemental sulfur. The mechanism of the Peachey process of rubber vulcanization is examined on the basis of concepts of the role of intermediate products of the reaction - free radicals.

2. Sulfur is found to react with many vulcanization accelerators with formation of considerable amounts of hydrogen sulfide. It is shown that hydroxycarbonyl compounds, which reduce sulfur to hydrogen sulfide, play the part of accelerators of sulfur vulcanization. Thermal breakdown of hydrogen persulfide leads to vulcanization of rubber.

3. The experimental data are applied to the consideration of the mechanism of the action of accelerators of sulfur vulcanization and of the mechanism of formation of mono- and polysulfide bonds.

LITERATURE CITED

[1] B. A. Dolgoplosk et al., Symposium: Vulcanization of Rubber (State Chem. Press, 1954), 51.

[2] Peachey and Skypsey, J. Soc. Chem. Ind. 40, 5 (1921).

[3] Fischer, Ind. Eng. Chem. 31, 1381 (1939).

[4] Zapp, Ind. Eng. Chem. 40, 1508 (1948).

[5] Mayo and Walling, Chem. Revs. 27, 387 (1940).

[6] Jones and Reid, J. Am. Chem. Soc. 60, 2452 (1938).

[7] Sernic, Banes and Swaney, J. Am. Chem. Soc. 70, 1804 (1948).

[8] Hull, Olsen and France, Ind. Eng. Chem. 38, 1282 (1946).

[9] B. A. Dogadkin, Physics and Chemistry of Rubber (1947), 347, 348.

[10] B. A. Dolgoplosk et al., Collection of Reports of the Conference on Chemical Kinetics and Reactivity (Acad. Sci. USSR Press, 1955), 303.

[11] Reynold and Gotten, Ind. Eng. Chem. 42, 1905 (1950).

[12] B. A. Dogadkin et al., Symposium: Vulcanization of Rubber (1954), 7.

[13] E. I. Tinyakova et al., J. Gen. Chem. 25, 1387 (1955) (T.p. 1333).*

[14] Witby, Wellman and Floutz, Ind. Eng. Chem. 42, 445 (1950).

[15] Kern, Makromolek. Chem. 1, 249 (1948).

[16] S. S. Medvedev and E. M. Chilikina, J. Phys. Chem. 13, 1201 (1939).

[17] Kharash, J. Org. Chem. 13, 97 (1948).

* T.p. = C. B. Translation pagination.

[18] I. Ostromyslensky, J. Russ. Chem. Soc. 47, 1453 (1915).

[19] Bloch and Höhn, Ber. 41, 1975 (1908).

[20] Bell and Agruss, Ind. Eng. Chem., Anal. Ed. 13, 297 (1941).

[21] Westlake, Laquer and Smith, J. Am. Chem. Soc. 42, 436 (1920).

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REDUCTION WITH FORMIC ACID AND ITS DERIVATIVES

VI. SYNTHESIS OF N-CYCLOALKYLETHANOLAMINES

A. N. Kost and N. I. Stupnikova

It has been claimed in the patent literature [1] that heating of cyclohexanone with ethanolamine and formamide leads to a 65% yield of N-cyclohexylethanolamine, salts of which (with halogenated phenols) possess insecticidal activity [2]. We reacted cyclohexanone with ethanolamine and formic acid. The reaction went smoothly, especially in presence of nickel and cobalt, and the yield of N-cyclohexylethanolamine reached 90%. The same facile reaction also goes with 2-methyl-, 3-methyl- and 4-methylcyclohexanone, and with somewhat lower yields with cyclopentanone.

Cis- and trans-isomers of N-cycloalkylethanolamines could have been formed in the reaction of methylcyclohexanones with ethanolamine and formic acid, but we only succeeded in isolating one substance in each case (the configuration was not investigated).

EXPERIMENTAL

N-Cyclohexylethanolamine. 31 g (0.5 mole) ethanolamine and 100 ml (about 2 moles) 85% formic acid were heated in a flask with a Wurtz attachment, the water being distilled off until the temperature of the mixture reached 200°. The mixture was then cooled to 100° and 2 g skeletal nickel and 29.4 g (0.3 mole) cyclohexanone were added; the flask was fitted with a reflux condenser, and heated for 3 hours (gentle boiling); gradual addition was made of formic acid (30 g, i.e. about 0.5 mole). The reaction mass was decanted from the nickel, hydrolyzed by boiling 6 hours with 200 ml 10% hydrochloric acid, made strongly alkaline, and extracted 5 times with ether. After drying with sodium hydroxide, the ether was driven off and the residue twice distilled in vacuum to give 40.2 g (94%) N-cyclohexylethanolamine, b.p. 118-119° (11 mm); m.p. 42°.

Found %: N 9.61, 9.73. $C_8H_{17}ON$. Calculated %: N 9.78.

Picrate, m.p. 129° (from benzene and then from alcohol). Dinitro-o-cresolate, m.p.101° (from alcohol).

Literature data: b.p. 119° (11 mm); picrate, m.p. 129° (from alcohol) [3].

N-(2-Methylcyclohexyl)-ethanolamine. This was similarly prepared from 31 g (0.5 mole) ethanolamine, 33.7 g (0.3 mole) 2-methylcyclohexanone and 130 g formic acid. Yield 36.1 g (77%), b.p. 105-115° (8 mm). Three fractionations in vacuum gave 28.5 g substance.

B.p. 114-115° (7 mm), 117-118° (9 mm), n_D^{20} 1.4830, d_4^{20} 0.9719, MR_D 46.27; calc. 46.69.
Found %: N 8.81, 8.89. $C_9H_{19}ON$. Calculated %: N 8.91.

The dinitro-o-cresolate is an oil. The picrate was obtained by mixing the benzene solutions; m.p. 114° (does not alter when recrystallized from benzene or alcohol).

N-(3-Methylcyclohexyl)- ethanolamine. Similarly prepared from 33.7 g (0.3 mole) 3-methylcyclohexanol, 31 g ethanolamine and 130 g formic acid. Yield 35.3 g (75%), b.p. 110-125° (10 mm). Three distillations in vacuum gave 28.4 g substance.

B.p. 118-119° (5 mm), n_D^{20} 1.4779, d_4^{20} 0.9600, MR_D 46.34; calc. 46.69.
Found %: C 68.78, 68.87; H 12.16, 12.29. $C_9H_{19}ON$. Calculated %: C 68.74; H 12.18.

The dinitro-o-cresolate and the benzoyl derivative are oily substances. The picrate melts at 85° after two recrystallizations from benzene, and the m.p. does not alter after further recrystallization from alcohol or benzene.

N-(4-Methylcyclohexyl)-ethanolamine. Prepared similarly from 31.0 g (0.28 mole) 4-methylcyclohexanone. Yield 33.9 g (77%) substance. Three distillations in vacuum gave 27.9 g N-(4-methylcyclohexyl)-ethanolamine.

B.p. 120° (5 mm), n_D^{20} 1.4774, d_4^{20} 0.9547, MR_D 46.56; calc. 46.69.
Found %: C 68.69, 68.73; H 12.13, 12.21. $C_9H_{19}ON$. Calculated %: C 68.74; H 12.18.

Picrate, m.p. 109° (from benzene).

N-(Cyclopentyl)-ethanolamine. Prepared similarly from 0.43 mole cyclopentanone and 0.6 mole ethanolamine. Yield 37.2 g (67.7%), b.p. 109-115° (15 mm). After redistillation:

B.p. 114-115.5° (10 mm), n_D^{20} 1.4828, d_4^{20} 0.9942, MR_D 37.12; calc. 37.45.

Picrate, m.p. 119° (from alcohol).

Found %: N 15.27, 15.34. $C_{13}H_{18}O_9N_4$. Calculated %: N 15.38.

SUMMARY

The synthesis of a series of N-cycloalkylethanolamines by the action of formic acid and ethanolamine on the corresponding cyclanones is described.

LITERATURE CITED

[1] U.S. Patent 2251245 (1941); C. A. 35, 6975 (1941).

[2] U.S. Patent 2382976 (1945); C.A. 40, 1543 (1946).

[3] E. Wedekind and E. Bruch, Ann. 471, 92 (1929).

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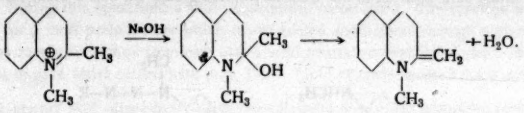
THE STRUCTURE OF THE PRODUCTS OF ALKALI TREATMENT OF QUATERNARY SALTS OF BENZIMIDAZOLE DERIVATIVES

B. A. Porai-Koshits and Kh. L. Muravich

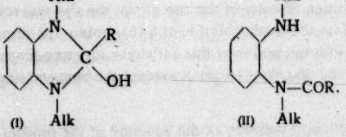
The reaction of alkalies with quaternary ammonium salts is of great interest because it leads, in a number of cases, to the little studied phenomenon of so-called "slow neutralization" in which, in place of a quaternary base, a neutral compound is formed containing a hydroxyl group covalently bound to the carbon atom. This phenomenon is also observed when the quaternary nitrogen atom is linked by a conjugated system of bonds with a coordinatively unsaturated carbon atom.

For example, aminotriarylmethane dyes are converted by caustic alkalies into triarylcarbinols. Formation of the latter was a basis for the assumption that aminotriarylmethane dyes are carbonium, and not ammonium salts [1]. This problem cannot be said to be conclusively solved. The action of alkalies on quaternary quinaldinium salts leads to an analogous reaction, in which the hydroxyl is possibly at first covalently bound to the carbon, and is then split off as water with the hydrogen of a methyl group to form 2-methylene-N-methylquinoline [2]:



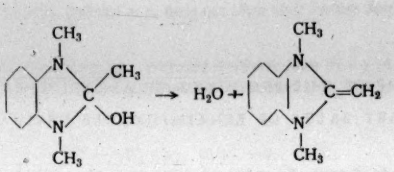
Formation of an intermediate carbinol compound has not been strictly proved.

The reaction of alkalies with quaternary alkylbenzimidazolinium salts is also apparently analogous. A neutral compound is formed which reversibly changes into a quaternary salt [3]. This led to the assumption that the neutral compound had the carbinol structure (I) [4]. Recently, however, this formula has been disputed in a number of papers: spectroscopic studies indicate the presence of an amido group in the substance. The structure (II) is therefore proposed for these substances as a result of opening of the imidazole ring during the reaction [5].

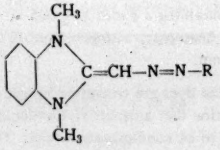


The problem of the structure of the products of interaction of caustic alkalies with quaternary benzimidazolinium salts was approached in the present work by investigation of the behavior of the product of treatment of 1,2-dimethylbenzimidazole in the azo coupling reaction.

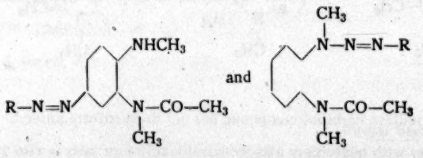
It seemed fairly obvious that a product with structure (I) could not enter into this reaction unless we make the improbable assumption of rupture of the heterocycle by the diazo compound. But, if we accept the possibility of separation of water with formation of a product similar to methylene-methylquinoline (see above), then



the azo group might enter the methylene group (as is the case in the quinoline series), with formation of an azo dye of the structure:



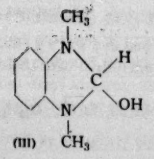
At the same time a product of structure (II) could give not only an azo dye with entry of the diazo group into the benzene ring in the para position to the secondary amido group, but also a diazoamino compound:



On treating the investigated substance with the p-nitrophenyldiazo compound, we satisfied ourselves that it reacts with facility with formation of two products – a yellow one and a red one. The properties of the yellow product (formation of a diazo compound on treatment with hydrochloric acid, ability to couple with β-naphthol and other azo components after treatment with mineral acid, etc.) indicated it to be a typical diazoamino compound. The red one, on the other hand, is an azo dye.

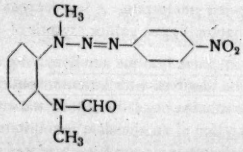
In order to establish the position of entry of the azo group, the dye was reduced in a hydrochloric acid medium, and thereby converted into the methochloride of 5 (6)-amino-1,2-dimethylbenzimidazole. This amine was found to be identical with the amine of this authentic structure prepared from the 5(6)-nitrobenzimidazole derivative. It was thus proved that the azo group entered the benzene ring in the reaction with the diazo compound.

For further confirmation, although indirect, of the structure of the product of alkali treatment of 1,2-dimethylbenzimidazole methiodide, we decided to subject to the azo-coupling reaction an analog of this compound, but one not containing a methyl group in the 2-position – the product of alkali treatment of 1-methylbenzimidazole methiodide. If the product in this case had the carbinol structure (III), it should not have been able to enter into the azo-coupling reaction, since its transformation into the methylene derivative is impossible.



(III)

As our experiments showed, however, the substance in question entered with facility into reaction with the p-nitrophenyldiazo compound with formation of a diazoamino compound whose properties, as well as the analytical data, are in harmony with the formula



The azo dye itself is only formed in minute yield in this reaction.

EXPERIMENTAL

Preparation of N-acetyl-N,N'-dimethyl-o-phenylenediamine. 5.8 g of 1,2-dimethylbenzimidazole methiodide was dissolved by heating in 50 ml water. Into the hot solution was gradually run 50 ml 40% sodium hydroxide solution. During this operation, a white precipitate came down. The reaction was completed by boiling the mixture for a short period, after which it was cooled and filtered through a glass filter. The precipitate on the filter was carefully washed free from alkali until neutral to phenolphthalein. It was crystallized from methyl alcohol to give white prisms with m.p. 164°. Yield of crude product 3.4 g (94%).

Coupling of N-acetyl-N,N'-dimethyl-o-phenylenediamine with p-nitrodiazobenzene. a) Coupling in ethereal suspension. 8.9 g of finely pulverized N-acetyl-N,N'-dimethyl-o-phenylenediamine was suspended in 100 ml ether. A diazo solution, prepared by diazotizing 7 g p-nitroaniline was added to the suspension, with constant stirring. The addition could be made fairly quickly at room temperature. With progressive addition of the diazo solution, the mixture first turned yellow and then deep red. At the same time, much solid came down, and the suspension became viscous. After all the diazo solution had been added, the mixture was transferred to a separating funnel and shaken for a short time for better mixing of the ethereal and aqueous layers. In this manner, the whole of the precipitate was brought into the aqueous layer, and the ether layer became yellow. After the layers had been separated, the ethereal solution was evaporated to leave a residue of yellow crystalline substance; this was recrystallized from a small amount of methyl alcohol to give a pure product with m.p. 120-121°.

The yellow substance dissolves readily in dilute hydrochloric acid, and the solution immediately acquires a pink-crimson color. Addition of sodium acetate in slight excess causes the color to change to yellow. On running this solution into an alkali solution of β-naphthol, a bright-red precipitate of azo dye comes down at once. This solution likewise reddens cloth impregnated with any azotol. Judging by all these properties, the yellow substance is a diazoamino compound, and this is confirmed by the analytical data:

Found %: C 58.79, 58.51; H 5.47, 5.3; N 21.48, 21.3. $C_{16}H_{17}O_3N_5$. Calculated %: C 58.72; H 5.2; N 21.4.

The red precipitate of dye in the aqueous layer was filtered and washed with water. After drying, the product is a red-orange powder which, on close inspection, is seen to be heterogeneous. A part of the product is appreciably soluble in cold methyl or ethyl alcohol, and separates therefrom, on dilution with water, in the form of an orange-yellow precipitate. Several recrystallizations from a small volume of methyl alcohol in presence of animal charcoal give yellow crystals with m.p. 120°, fully identical with the diazoamino compound isolated

from the ethereal solution. The residue, insoluble in cold alcohol, was crystallized from a large volume of ethyl or methyl alcohol. The pure product forms dark red, lustrous plates with m.p. 189°.

The total yield of diazoamino compound and dye was 9 g (55.1%). Fractionation of the product gives 6.5 g diazoamino compound and 2 g dye. The analytical data indicate the following composition:

Found %: C 58.6, 58.56; H 5.32, 5.36; N 21.53, 21.57. $C_{16}H_{17}O_3N_5$. Calculated %: C 58.72; H 5.2; N 21.4.

b) Coupling in methanol solution. 3.6 g N-acetyl-N,N'-dimethyl-o-phenylenediamine was dissolved in 150 ml methanol. The solution was cooled to 5°, and a solution of p-nitrodiazobenzene prepared by diazotization of 2.8 g p-nitroaniline was slowly added, with constant stirring. The solution turned red at first, but toward the end of the addition of the diazo component, a small amount of red solid came down. The latter was filtered, dried and crystallized from ethyl or methyl alcohol. Yield of crude product 0.36 g; m.p. 189°. Dilution of the filtrate with water brought down an orange-red precipitate. A few recrystallizations from a small amount of methyl alcohol (with addition of animal charcoal) gave yellow crystals of diazoamino compound with m.p. 120°.

Transformation of the diazoamino compound into the azo dye. 5 g diazoamino compound was mixed with 10 ml 80% formic acid. The compound dissolved with instantaneous change of color of the solution which became dark-red. After 5-10 minutes, the solution began to deposit red crystals and, in the course of a few seconds, the mixture thickened due to separation of an abundant precipitate. The mass was diluted with methanol, and the crystals were filtered. The precipitate on the filter was washed with methanol, then with ether for complete removal of unreacted diazoamino compound. The pure azo dye was obtained with m.p. 189°. Yield 3 g (60%).

Reduction of the azo dye. 5 g of dye was dissolved in 200 ml hydrochloric acid (d 1.19), the solution was heated, and granulated tin was gradually added. At the start the solution became deep crimson and, with continued heating, a red-brown precipitate came down. After addition of the tin, the precipitate gradually dissolved. Toward the end the solution became transparent and completely colorless. Cooling of the solution resulted in separation of a white amorphous precipitate. It was filtered, dissolved in 400 ml water, and acidified with hydrochloric acid; the tin was brought down with hydrogen sulfide. The tin sulfide was filtered and washed with water, and the filtrate was evaporated to dryness in a porcelain dish on a water bath.

The residue after evaporation was a mixture of two amines – p-phenylenediamine hydrochloride and 1,2-dimethyl-5(6)-aminobenzimidazole methochloride. The components were separated by treating the mixture with concentrated hydrochloric acid (d 1.19), in which p-phenylenediamine hydrochloride is substantially insoluble. The latter was filtered off and the filtrate again evaporated to dryness. The residue was extracted with cold ethyl alcohol and filtered, and from the filtrate a product with m.p. 263° was precipitated by ether. The product was freed from traces of p-phenylenediamine by extraction with alcohol and reprecipitation with ether, the operation being repeated several times. The product forms colorless needles, readily soluble in water and less soluble in cold alcohol. M.p. 298°.

Preparation of N-acetyl-N,N'-dimethyl-4(5)-nitro-o-phenylenediamine. Two methods may be employed for this preparation. a) An aqueous solution of 1,2-dimethyl-5(6)-nitrobenzimidazole methiodide was treated, while gently heating, with 40% sodium hydroxide solution. The resultant yellow precipitate was crystallized from alcohol. According to the literature the m.p. is 175°. Our product started to darken at 175°, subsequently began to decompose, and finally melted at 185°.

b) The method of synthesis described in the literature starts from N,N'-dimethyl-4(5)-nitro-o-phenylenediamine. The latter was prepared by hydrolysis of 1-methyl-5(6)-nitrobenzimidazole methiodide, which goes with great facility in presence of cold caustic alkali. N,N'-Dimethyl-4(5)-nitro-o-phenylenediamine was treated with cold acetic anhydride instead of the mixture of acetic anhydride and acetic acid at the boil recommended in the literature [6]. Treatment with acetic anhydride leads to heat development and gradual change of color from red to light yellow. After recrystallization from alcohol, the product has the same melting point as the product obtained by the first method.

Reduction of N-acetyl-N,N'-dimethyl-4(5)-nitro-o-phenylenediamine. 2.5 g of the product obtained by one of the above methods was dissolved in 100 ml hydrochloric acid (d 1.19), and reduced with granulated

tin while heating. The solution decolorized as the heating progressed, and a white amorphous precipitate came down on cooling. This was filtered and dissolved in water; 5-10 ml hydrochloric acid was added, and the tin was brought down with hydrogen sulfide. The precipitated tin sulfide was filtered off, the filtrate was evaporated to dryness, and the residue was crystallized from ethyl alcohol. Recrystallization from a small quantity of ethyl alcohol, or reprecipitation with ether from cold alcohol, gave a product with m. p. 298°.

The melting point of this product, obtained by a slightly different method of reduction, was 295° [7].

N-Formyl-N,N'-dimethyl-o-phenylenediamine. The starting substance for this preparation was 1-methylbenzimidazole methiodide. The latter was obtained by the following method: 5.12 g benzimidazole was heated in a sealed tube with 8 ml methyl iodide and 10 ml methyl alcohol for 4-6 hours at 140°. After the tube had been opened, its contents (crystals) were extracted with ethyl alcohol, filtered and washed with ether. Yield of product 11.8 g (90%).

The methiodide was dissolved in 200 ml water, the solution was heated, and 100 ml 40% sodium hydroxide solution was added; during the latter operation the solution at first became turbid, and then an oil separated. The latter was extracted with ether and the ethereal layer was separated from the aqueous layer. The ethereal layer was dried over freshly ignited calcium chloride and then evaporated. The white product was crystallized from ligroine. M.p. 74-75°; yield of crude product 5.6 g (79%). Appreciable darkening occurred on standing.

Coupling of N-formyl-N,N'-dimethyl-o-phenylenediamine with p-nitrodiazobenzene. 3.3 g N-formyl-N,N'-dimethyl-o-phenylenediamine was dissolved in 20 ml ether, and the solution was cooled to 0° before dropwise addition of the diazo solution, prepared from 2.8 g p-nitroaniline. Care was taken that the temperature did not rise above 5°. The solution turned red as the p-nitrodiazobenzene was added, and later a resinous precipitate was formed. The reddish-brown precipitate was filtered, washed with ether and dried. Yield of product 3.0 g (43%). Recrystallization from a small quantity of methanol gave reddish-brown crystals which, however, were not uniformly colored. Closer inspection revealed that the red-brown color was merely superficial (adsorbed from solution). The crystals became appreciably paler when triturated. Several recrystallizations from methanol in presence of animal charcoal gave light yellow acicular crystals with m.p. 119°.

The substance dissolved in dilute hydrochloric acid with a red-crimson color. After neutralization with sodium acetate, it was coupled with β-naphthol in alkali solution. This behavior indicated that the product is a diazoamino compound. An attempt to convert it into an azo dye, however, was unsuccessful. On treatment with formic or acetic acid, the substance went into solution with a red color, but no product of any kind could be isolated. Nor could a dye be isolated from the crude product obtained by coupling. The dye is evidently only formed in very small quantity, as evidenced by the deep color of the solution obtained, both during the coupling and during dissolving of the diazoamino compound in acids.

Found %: C 57.4, 57.28; H 4.9, 4.94; N 22.37, 22.5. $C_{16}H_{15}O_3N_5$. Calculated %: C 57.51; H 4.79; N 22.36.

SUMMARY

Judging by their ability to enter into reaction with diazo compounds with formation of diazoamino compounds and azo dyes, the products of alkali treatment of the methiodides of 1,2-dimethyl- and 1-methylbenzimidazoles are not carbinol compounds, but acetyl- and formyl-dimethyl-o-phenylenediamines (symmetrical). Consequently, the alkali treatment of quaternary salts of benzimidazole compounds leads to opening of the imidazole ring.

LITERATURE CITED

[1] R. Vitsinger, Organic Dyes (United Sci.-Tech. Press, 1936), 18.

[2] W. Kŏnig, Ber. 57, 891 (1924); W. Kŏnig, Ber. 56, 1543 (1923).

[3] O. Fischer, J. prakt. Chem. (2) 73, 419 (1898).

[4] S. Niementowski, Ber. 20, 1886 (1887); O. Fischer and W. Hess, Ber. 36, 3967 (1903).

[5] C. W. Smith, R. S. Rasmussen and S. A. Ballard, J. Am. Chem. Soc. 71, 1084 (1949); A. M. Simonov and F. A. Mendelevich, J. Gen. Chem. Suppl. Vol. II, 1387 (1954).

[6] O. Fischer and W. Hess, Ber. 36, 3968 (1903).

[7] M. A. Phillips, J. Chem. Soc. 1931, 1143.

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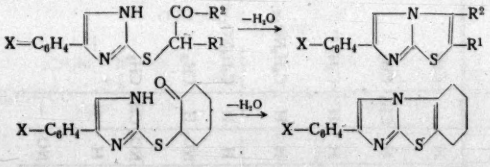
INVESTIGATIONS IN THE IMIDAZOLE SERIES

V. THE ACTION OF PHOSPHORUS OXYCHLORIDE AND OF ACETIC AND PHOSPHORIC ACIDS ON 2-β-KETOALKYL(ARYL)-MERCAPTOIMIDAZOLES

P. M. Kochergin

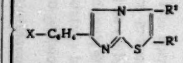
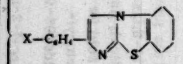
It was previously established that some 4(5)-phenyl-2-β-ketoalkyl(aryl)-mercaptoimidazolescyclizeto substituted imidazo-(2,1-b)-thiazoles on heating with hydrochloric [1] or sulfuric [2, 3] acid, or on boiling their hydrochlorides in butyl alcohol [1]. These reagents cannot be used in all cases because the hydrohalides of some 2-β-ketoalkyl(aryl)-mercaptoimidazoles are nearly insoluble in butyl alcohol, and hydrochloric acid (at the boiling point) and sulfuric acid (at 30-50°) do not cyclize some compounds. At higher temperatures (95-100°) sulfuric acid, apart from its cyclizing action, leads to sulfonation of the benzene ring of phenylimidazo-(2, 1-b)-thiazoles or of phenylimidazo-(2, 1-b)-tetrahydrobenzothiazoles [3]. The literature also mentions the use of glacial acetic acid for cyclization of 2-acetonyl-mercaptobenzimidazole [2] and of phosphorus oxychloride for cyclization of 2-acetonyl-mercaptoimidazoles [4, 5] and 2-acetonylmercaptopurines [4, 6], but the action of these reagents has not been adequately studied. No reference to the action of phosphoric acid on 2-β-ketoalkyl-mercaptoimidazoles has appeared in the literature.

In the present work the cyclization of all the previously obtained 4(5)-phenyl- and 4(5)-p-nitrophenyl-2-β-ketoalkyl(aryl)-mercaptoimidazoles [1] to the corresponding imidazo-(2, 1, b)-thiazoles and imidazo-(2, 1-b)-tetrahydrobenzothiazoles was realized, and the possibility of application of phosphorus oxychloride and acetic and phosphoric acids as dehydrating agents was studied.



It was establishedthat the susceptibility to cyclization of 2-β-ketoalkyl(aryl)-mercaptoimidazoles with formation of imidazo-(2,1-b)-thiazoles differs for various S-β-ketoalkyl(aryl) groups. 2-β-Ketoalkylmercapto-imidazoles in which the radicals linked to sulfur are residues of fatty or alicyclic ketones are readily cyclized by boiling with glacial acetic acid for 4-5 hours or with 85% phosphoric acid when heated at 95-100° for 1 hour. These reagents act on S-acetonyl-, methylacetonyl- and cyclohexanonyl derivatives of 4(5)-phenyl-2-mercapto-imidazole to give good yields (90-98.5%) of the corresponding cyclic compounds I, II and VIII (see table).

S-substituted 4(5)-phenyl-2-mercaptoimidazoles containing residues of aliphatic-aromatic ketones (phenacyl, p- and m-nitrophenacyl) do not cyclize on boiling with acetic acid or on heating to 100° with phosphoric acid. Failure also attended the attempt to cyclize 4(5)-phenyl-2-phenacylmercaptoimidazole with the help of phosphorus pentoxide. The compound did not cyclize when boiled in anhydrous xylene for 2 hours in presence of 9 times its weight of phosphorus oxychloride. At the boiling point, phosphorus oxychloride easily cyclizes 2-β-

№	General formula	X	R^1	R^2	Yield % with reagents: CH_3COOH	H_3PO_4	POCl_3	Color and form of crystals*	Melting point	Molecular weight	Empirical formula	Calculated %: C	H	N	S	Found***%: C	H	N	S
I		H		CH_3	98.3	97.8	98	Colorless prisms	113—113.5°	214.15	$C_{12}H_{10}N_2S$	—	—	—	—	—	—	—	—
II		H	CH_3	CH_3	92	90	—	Colorless plates	157—158	228.16	$C_{13}H_{12}N_2S$	—	—	—	—	—	—	—	—
III		H	H	C_6H_5 **	—	—	95.3	Colorless prisms	125—125.5	276.16	$C_{17}H_{12}N_2S$	73.87	4.38	10.13	11.61	74.06	4.41	9.88	11.48
IV		H	H	$C_6H_4NO_2$-p	—	—	96.5	Yellow crystals	210.5—211.5	321.17	$C_{17}H_{11}O_2N_3S$	63.51	3.45	13.07	9.98	63.55	3.66	13.06	10.22
V		H	H	$C_6H_4NO_2$-m	—	—	80	Yellow prisms	156.5—157	321.17	$C_{17}H_{11}O_2N_3S$	63.51	3.45	13.07	9.98	63.41	3.46	13.00	9.70
VI		NO_2	H	CH_3	—	—	97.7	Yellow plates	246	259.12	$C_{12}H_9O_2N_3S$	—	—	16.21	—	—	—	16.08	—
VII		NO_2	CH_3	CH_3	—	—	86	Yellow prisms	248—248.5	273.17	$C_{13}H_{11}O_2N_3S$	57.11	4.06	15.38	11.73	57.17	3.96	15.31	11.61
VIII		H	—	—	96.2	96.7	98.5	Colorless needles	169	254.18	$C_{15}H_{14}N_2S$	—	—	—	—	—	—	—	—
IX		NO_2	—	—	—	—	98.5	Yellow prisms	233—234	299.18	$C_{15}H_{13}O_2N_3S$	60.16	4.38	14.05	10.72	59.92	4.38	13.86	10.75

* Compounds I, II, III, V, VI and VIII were recrystallized from alcohol, IV, VII and IX from glacial acetic acid.

** Hydrochloride: colorless prisms from alcohol, m.p. 201-202°. Found %: Cl 11.47. $C_{17}H_{13}N_2ClS$. Calculated %: Cl 11.34.

*** All analyses were made in the microanalytical laboratory of the All-Union Institute of Pharmaceutical Research under the guidance of V. V. Kolpakova.

ketoalkyl(aryl)-mercaptoimidazoles regardless of the character of the ketonic residue. In the case of 4(5)-phenyl-2-β-ketoalkylmercaptoimidazoles, where the β-ketoalkyl radicals are residues of fatty or alicyclic ketones, ring closure occurs on boiling for $^1/_4$-1 hour. In the case of S-derivatives of fatty-aromatic ketones, cyclization under the influence of phosphorus oxychloride takes places after more prolonged boiling (10-18 hours).

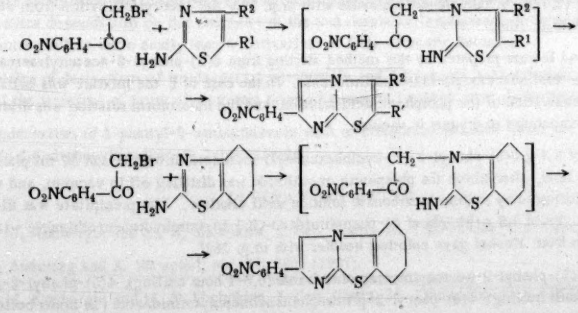
In the table are set forth the properties of bicyclic and tricyclic compounds prepared by the action of phosphorus oxychloride, acetic acid and phosphoric acid on 4(5)-phenyl- and 4(5)-p-nitrophenyl-2-β-ketoalkyl(aryl)-mercaptoimidazoles. Reduction of 3-m-nitrophenyl-6-phenylimidazo-(2,1-b)-thiazole (V) in alcoholic ammoniacal solution with hydrogen sulfide gave 3-m-aminophenyl-6-phenylimidazo-(2,1-b)-thiazole (X), which was characterized as the dihydrochloride.

As indicated previously [1], cyclization of 4(5)-phenyl-2-β-ketoalkyl(aryl)-mercaptoimidazoles should theoretically give two isomers: 5-phenyl- and 6-phenylimidazo-(2,1-b)-thiazoles, while imidazo-(2,1-b)-tetrahydrobenzothiazoles could give 9-phenyl- and 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazoles. For the series of compounds (I and II) it was shown that the phenyl group in them is in the 6-position of the imidazo-(2,1-b)-thiazole bicycle, and in the case of the tricyclic compound (VIII) it is in the 10-position of the imidazo-(2,1-b)-tetrahydrobenzothiazole tricycle.

In the present work we established that also in the cyclization of 4(5)-p-nitrophenyl-2-β-ketoalkylmercaptoimidazoles the p-nitrophenyl group is likewise in the 6-position in the imidazo-(2,1-b)-thiazole bicycle or correspondingly in the 10-position in the inidazo-(2,1-b)-tetrahydrobenzothiazole tricycle, as was proved by reverse synthesis of a series of compounds from thiazole derivatives.

Condensation of 2-amino-4,5,6,7-tetrahydrobenzothiazole, 4,5-dimethyl-2-aminothiazole and 4-methyl-2-aminothiazole with α-bromo-p-nitroacetophenone gave respectively 10-p-nitrophenylimidazo-(2,1-b)-tetrahydrobenzothiazole, 2,3-dimethyl-6-p-nitrophenylimidazo-(2,1-b)-thiazole and 3-methyl-6-p-nitrophenylimidazo-(2,1-b)-thiazole (IX, VII and VI). Compound VI has been described in the literature [7]. These compounds were identical with those synthesized by cyclization of the corresponding 4(5)-p-nitrophenyl-2-β-ketoalkylmercapto-imidazoles (see Scheme 1).

Scheme 1.



We did not confirm the structure of Compounds III, IV and V by reverse synthesis from the corresponding 2-aminothiazoles and α-bromoacetophenone, but by analogy with other imidazo-(2,1-b)-thiazoles (I, II, VI and VII) it could be assumed that the phenyl group in them is likewise in the 6-position of the imidazo-(2,1-b)-thiazole bicycle. However, we attempted to prepare 3,6-diphenylimidazo-(2,1-b)-thiazole (III) from 4-phenyl-2-aminothiazole [8]. It was observed that condensation of 4-phenyl-2-aminothiazole with α-bromoacetophenone in ethyl or butyl alcohol or benzene followed by distillation of the solvent and boiling of the residue with glacial acetic acid did not lead to formation of 3,6-diphenylimidazo-(2,1-b)-thiazole. A negative result was also obtained when the condensation was attempted in anhydrous ethyl alcohol in presence of an equivalent amount of sodium ethoxide followed by separation of the sodium bromide, distillation of the solvent and boiling of the residue with glacial acetic acid. In all experiments the starting substances (4-phenyl-2-aminothiazole and α-bromoacetophenone)

were recovered unchanged together with 4-phenyl-2-aminothiazole hydrobromide (due to partial decomposition of α-bromoacetophenone). In none of the experiments was the desired 3,6-diphenylimidazo-(2,1-b)-thiazole obtained.

The difference in reactivity of 4-phenyl-2-aminothiazole in comparison with that of other 2-aminothiazoles is evidently due to the influence of the phenyl group in the 4-position of the thiazole ring and to the resultant difficulty of alkylation by α-bromoacetophenone of the ring nitrogen atom. This explanation is also supported by the fact that condensation of 2-aminothiazoles with α-haloketones is not a general method of preparation of imidazo-(2,1-b)-thiazoles.

All the compounds prepared, with exception of VII and IX, as well as I, II and VIII (whose action was reported on previously [1]), were tested at the All-Union Institute of Pharmaceutical Chemical Research for antibacterial activity (range of 16 types of microbes).* No highly active compounds were found.

We convey cordial thanks to M. N. Shchukina for her constant interest and valuable advice when this work was being undertaken.

EXPERIMENTAL

10-Phenylimidazo-(2,1-b)-tetrahydrobenzothiazole (VIII).

a) A solution of 1.5 g 4(5)-phenyl-2(2'-cyclohexanonyl)-mercaptoimidazole in 10 ml glacial acetic acid was boiled 4½ hours, and the acetic acid was then distilled off in vacuum. The oily residue, which crystallized on cooling, was dissolved in 10 ml boiling alcohol and the crystalline mass which separated after cooling was filtered, washed with 5 ml ether, and dried. A further small quantity of this substance was recovered by evaporating the alcohol-ethereal mother liquor. Yield 1.26 g (96.2%) of 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole with m.p. 168-169°. After recrystallization from alcohol the colorless needles had m.p. 169°. Compounds I and II were prepared by this method, starting from 4(5)-phenyl-2-acetonylmercaptoimidazole and 4(5)-phenyl-2-(α-methylacetonyl)-mercaptoimidazole.

b) A mixture of 1 g 4(5)-phenyl-2-(2'-cyclohexanonyl)-mercaptoimidazole and 10 ml 85% phosphoric acid was heated on a boiling water bath for 1 hour, after which the solution was cooled and neutralized with sodium bicarbonate solution. The white precipitate was filtered, washed with water and dried. Yield 0.9 g (96.7%) of 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole with m.p. 165-168°; recrystallization from alcohol gave colorless needles with m.p. 169°.

Compounds I and II were prepared by this method, starting from 4(5)-phenyl-2-acetonylmercaptoimidazole and 4(5)-phenyl-2-(α-methylacetonyl)-mercaptoimidazole. In the case of I, the mixture was extracted with chloroform after neutralization of the phosphoric acid solution, and the chloroform solution was dried with potassium carbonate and evaporated to dryness in vacuum.

c) A mixture of 3.7 g 4(5)-phenyl-2-(2'-cyclohexanonyl)-mercaptoimidazole and 37 ml phosphorus oxychloride was boiled 1 hour, after which the phosphorus oxychloride was distilled off in vacuum, and water was added to the residue followed by sodium bicarbonate solution until alkaline. The precipitate was filtered, washed with water and dried. Yield 3.3 g (98.5%) of 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole with m.p. 162-165°; recrystallization from alcohol gave colorless needles with m.p. 169°.

Starting from 4(5)-phenyl-2-acetonylmercaptoimidazole (0.5-1 hour boiling), 4(5)-phenyl-2-phenacylmercaptoimidazole (10 hours boiling), 4(5)-phenyl-2-p-nitrophenacylmercaptoimidazole (18 hours boilding), 4(5)-phenyl-2-m-nitro-phenacylmercaptoimidazole (17 hours boiling), 4(5)-p-nitrophenyl-2-acetonylmercaptoimidazole (8.5 hours boiling); 4(5)-p-nitrophenyl-2-(α-methylacetonyl)-mercaptoimidazole (1.4 hours boiling) and 4(5)-p-nitrophenyl-2-(2'-cyclohexanonyl)-mercaptoimidazole (30 minutes boiling), preparations were effected, respectively, of Compounds I, III-VII and IX. Ring closure of 2-β-ketoalkyl(aryl)-mercaptoimidazoles containing a nitro group was effected with phosphorus oxychloride in the proportion of 20 ml per gram of starting substance.

3-m-Aminophenyl-6-phenylimidazo-(2,1-b)-thiazole (X). A stream of hydrogen sulfide was passed for 3 hours at room temperature into a solution of 0.45 g 3-m-nitrophenyl-6-phenyl-imidazo-(2,1-b)-thiazole in 50 ml alcohol and 4 ml aqueous ammonia (d 0.92). The reaction mass was then refluxed for 1 hour, the solvent was

* The investigations were undertaken by S. N. Milovanova and A. A. Mikerina under the direction of G. N. Pershin.

distilled off in vacuum, and the residue treated with anhydrous acetone. The acetone solution was filtered and evaporated to dryness, the solid residue was dissolved in 100 ml hot 10% hydrochloric acid, and the solution was filtered and evaporated in vacuum to a volume of 25-30 ml. A crystalline precipitate came down on cooling and was filtered and dried. Yield 0.5 g (89.3%) of the dihydrochloride of 3-m-aminophenyl-6-phenylimidazo-(2,1-b)-thiazole with m.p. 236-250° (decomp.); recrystallization from alcohol gave colorless, fine needles with m.p. 257-260° (with decomp. in sealed capillary), soluble in alcohol and sparingly soluble in cold water.

Found %: C 51.17; H 4.74; N 10.75; S 8.00; Cl 17.21; H_2O 10.32.
$C_{17}H_{15}N_3Cl_2S \cdot 2H_2O$. Calculated %: C 50.98; H 4.78; N 10.50; S 8.01; Cl 17.72; H_2O 9.00.

2,3-Dimethyl-6-p-nitrophenylimidazo-(2,1-b)-thiazole (VII). A solution of 5.9 g α-bromo-p-nitroacetophenone and 3.1 g 4,5-dimethyl-2-aminothiazole in 45 ml alcohol was boiled for 2 hours. After cooling of the reaction mass, the precipitate was filtered, washed with alcohol and then with ether, and dried. An additional crop of this substance was obtained by adding ether to the mother liquor. Yield 8 g (91.1%) of the hydrobromide of 2,3-dimethyl-6-p-nitrophenylimidazo-(2,1-b)-thiazole. The base – 2,3-dimethyl-6-p-nitrophenylimidazo-(2,1-b)-thiazole – was isolated by treatment in alcohol with potassium carbonate. Yellow prisms from glacial acetic acid, m.p. 248-248.5°, sparingly soluble in alcohol, acetone, carbon tetrachloride, ethyl acetate and glacial acetic acid, almost insoluble in ether and gasoline, readily soluble in chloroform, benzene, dioxane and dichloroethane, insoluble in water and caustic alkali. A mixture with 2,3-dimethyl-6-p-nitrophenylimidazo-(2,1-b)-thiazole (VII, m.p. 248-248.5°), obtained from 4(5)-phenyl-2-(α-methylacetonyl)-mercaptoimidazole, melted at 248-248.5°.

Starting from 4-methyl-2-aminothiazole, 2-amino-4,5,6,7-tetrahydrobenzothiazole and α-bromo-p-nitroacetophenone, VI and IX respectively were prepared by this method; Yield 90-95%.

SUMMARY

1. The possibility of using phosphorus oxychloride, acetic acid and phosphoric acid for cyclization of 4(5)-phenyl- and 4(5)-p-nitrophenyl-2-β-ketoalkyl(aryl)-mercaptoimidazoles was studied. The most effective dehydrating agent in this reaction is phosphorus oxychloride; acetic and phosphoric acids are weaker.

2. It was established the susceptibility to cyclization of 2-β-ketoalkyl(aryl)-mercaptoimidazoles to imidazo-(2,1-b)-thiazoles depends also on the character of the S-β-ketoalkyl(aryl)group. S-Derivatives of fatty and alicyclic ketones cyclize more easily than S-derivatives of fatty-aromatic ketones.

3. A series of derivatives of imidazo-(2,1-b)-thiazole and imidazo-(2,1-b)-tetrahydrobenzothiazole was prepared, and the structure of some of them was proved by reverse synthesis from derivatives of 2-aminothiazole.

4. Condensation of 4-phenyl-2-aminothiazole with α-bromoacetophenone under the specified conditions did not yield 3,6-diphenylimidazo-(2,1-b)-thiazole.

LITERATURE CITED

[1] P. M. Kochergin and M. N. Shchukina, J. Gen. Chem. 26, 1723 (1956) (T.p. 1933).*

[2] H. Andersag and K. Westphal, Ber. 70, 2035 (1937).

[3] P. M. Kochergin and M. N. Shchukina, J. Gen. Chem. 26, 1733 (1956) (T.p. 1945).*

[4] E. Ochiai, Ber. 69, 1650 (1936).

[5] E. Ochiai and T. Y. Hou, J. Pharm. Soc. Japan 58, 33 (1938); Chem. Zentr. 1938, II, 859.

[6] E. Ochiai and S. Kitagawa, J. Pharm. Soc. Japan 56, 177 (1936); Chem. Zentr. 1937, I, 2974.

[7] T. Matsukawa and S. Ban, J. Pharm. Soc. Japan 71, 756 (1951); C. A. 46, 8094 (1952).

[8] R. M. Dodson and L. C. King, J. Am. Chem. Soc. 67, 2242 (1945).

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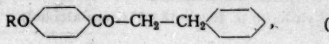
* T. p = C. B. Translation pagination.

PREPARATION OF p-HYDROXYPHENYL-PHENETHYL KETONE AND SOME OF ITS ETHERS AND HOMOLOGS

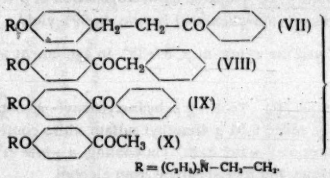
V. A. Zasosov, E. I. Metelkova and S. N. Milovanova

p-Hydroxyphenyl-phenethyl ketone (I) (4'-hydroxyhydrochalcone) has been unknown up to now. Known ethers of p-hydroxyphenyl-phenethyl ketone are p-methoxyphenyl-phenethyl ketone [1] and p-(β-diethylaminoethoxy)-phenyl-phenethyl ketone [2]. Both of these ethers were prepared by hydrogenation of the corresponding p-alkoxyphenyl-styryl ketones. We set out to develop a method for preparation of the base substance p-hydroxyphenyl-phenethyl ketone as a starting material for further syntheses. There is evidence for assuming that ethers of p-hydroxyphenyl-phenethyl ketone and ethers of some of its analogs can be of interest as therapeutic agents in the field of dermatology [3]. We prepared two series of derivatives of fatty-aromatic and aromatic ketones of the general formula:



(1 st series)

R = CH_3 (II), C_2H_5 (III), $(C_2H_5)_2N-CH_2-CH_2$ (IV), $(CH_3)_2N-CH_2-CH_2-CH_2$ (V).



(2nd series)

R = $(C_2H_5)_2N-CH_2-CH_2$.

We employed the following route for p-hydroxyphenyl-phenethyl ketone (I). Condensation of p-hydroxyacetophenone with benzaldehyde in presence of sodium hydroxide gave p-hydroxyphenyl-styryl ketone when following the procedure of Shriner and Kurosava [4] but with some modifications and simplifications. Phenyl-styryl ketones have been converted into phenyl-phenethyl ketones by reduction with zinc dust in acetic acid [5], sodium amalgam in 50% acetic acid [6], hydrogen over palladium chloride [7], platinum oxide [1] or palladium oxide [2] in a medium of acetone or alcohol. Reduction with the help of zinc dust or sodium amalgam did not give satisfactory results. We found that hydrogenation of p-hydroxyphenyl styryl ketone with hydrogen goes very smoothly and nearly quantitatively in presence of skeletal nickel catalyst in aqueous alkali solution at atmospheric pressure and room temperature.

p-Hydroxyphenethyl-phenyl ketone (VI) was similarly prepared by hydrogenation of p-hydroxystyryl-phenyl ketone, which is obtained by condensation of p-hydroxybenzaldehyde with acetophenone [4]. p-Hydroxyphenyl-benzyl ketone and p-hydroxybenzophenone were obtained by the literature methods [8, 9]. p-Hydroxyacetophenone, required for preparation of Compound (X) as well as for synthesis of p-hydroxyphenyl-styryl ketone, was prepared by the Fries reaction from phenyl acetate or by the diazo method from p-aminoacetophenone. The second method is more convenient for the preparation of larger quantities of this compound. Ethers of the respective hydroxyketones were prepared by treatment of the latter with a dialkyl sulfate in aqueous alkali solution or

or with alkyl halides in alcoholic alkali solution. Ethers containing the dialkylaminoalkoxy group were prepared in the form of the well-crystallizing citrates. All of the prepared compounds were tested as epitheliating media on experimental animals. Results of tests are set forth in Tables 1 and 2.

EXPERIMENTAL

1. p-Hydroxyphenyl-styryl ketone. 12.6 g sodium hydroxide was dissolved in 85 ml water and to the solution were added 20 g p-hydroxyacetophenone, 30 ml alcohol and 15.6 g benzaldehyde. The stirred mixture was heated at 70° for 2 hours, left at room temperature for 8 hours and then diluted with twice the volume of water. p-Hydroxyphenyl-styryl ketone was separated by slow addition of 10% hydrochloric acid until the reaction was acid to congo. The precipitated ketone was collected, washed with water and dried. Weight 31.5 g (93.4% calculated on the p-hydroxyacetophenone). M.p. 174-174.5°. According to the literature [4] p-hydroxyphenyl-styryl ketone melts at 173-174°. The absolutely pure substance was obtained by recrystallization from alcohol* in the ratio of 1 : 3.5. Yield about 75%. M.p. 177.5°.

2. p-Hydroxyphenyl-phenethyl ketone (I). 22.4 g p-hydroxyphenyl-styryl ketone was charged into a hydrogenation vessel and dissolved in 100 ml 1 N solution of sodium hydroxide; after complete solution, 2.5 g nickel catalyst was added. The vessel was twice swept with hydrogen and the apparatus was shaken until hydrogen ceased to be absorbed. About 2.3 liters hydrogen was taken up. The duration of hydrogenation was about 4 hours. The initially orange solution became light yellow after hydrogenation. The solution was filtered from catalyst and acidified with 10% hydrochloric acid. The colorless precipitate was filtered, washed with water and dried at 60-70°. Weight 22.5 g (99%), m.p. 104°. Colorless crystals, insoluble in water, soluble in alcohol, acetone and benzene; soluble in caustic alkalies with a yellowish color.

Treatment of the product with dimethyl sulfate in an alkaline medium gave the methyl ether with m.p. 96-97° and the oxime of this ether with m.p. 113-114°. The constants were in complete agreement with the literature data [1] for these substances prepared by another route.

3. p-Hydroxystyryl-phenyl ketone. Prepared similarly to p-hydroxyphenyl-styryl ketone from p-hydroxybenzaldehyde and acetophenone in 55.7% yield; m.p. 183.5-184.5° (from alcohol). The literature [4] gives m.p. 183-184°.

4. p-Hydroxyphenethyl-phenyl ketone (VI). Prepared by hydrogenation of p-hydroxystyryl-phenyl ketone, under the conditions specified for p-hydroxyphenyl-phenethyl ketone, in 99% yield. M.p. 116-117° (from alcohol).

The methyl ether had m.p. 63-64° and the oxime m.p. 87-88°, in agreement with the literature [1] for substances prepared by other routes.

5. p-Methoxyphenyl-phenethyl ketone (II). To 1.5 g p-hydroxyphenyl-phenethyl ketone, dissolved in about 5 ml 10% sodium hydroxide, was gradually added 0.91 g dimethyl sulfate while cooling with ice. After stirring, the reaction mass was heated 15-20 minutes on a water bath. On cooling, a white crystalline precipitate was obtained; this was filtered, washed with water and recrystallized from alcohol.

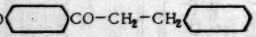
Yield 1.15 g (72.4%). M.p. 96-96.5°.

6. p-Ethoxyphenyl-phenethyl ketone (III). 10.5 g p-hydroxyphenyl-phenethyl ketone was dissolved in 50 ml alcohol containing 2.5 g sodium hydroxide. To the solution was added 7.26 g ethyl iodide, and the mixture was boiled 4 hours. The reaction mass was diluted with water and the product of reaction was extracted with ether. After drying the extract with potassium carbonate and driving off the ether, we distilled the residue in vacuum and a fraction boiling at 205° (1 mm) was collected. Weight 9.5 g (80.5%). Crystalline mass with freezing point 20°.

7. p-(β-Diethylaminoethoxy)-phenyl-phenethyl ketone (IV). 13.56 g p-hydroxyphenyl-phenethyl ketone (I) was dissolved in 60 ml alcohol containing 3 g sodium hydroxide, and the solution was stirred with 7.38 g diethylaminoethyl chloride. The mixture was boiled 4 hours. The sodium chloride (3.2 g compared with the theoretical amount of 3.48 g) was filtered off, the filtrate was diluted with water, and the reaction product was extracted with ether. The extract was dried with potassium carbonate, the ether was driven off, and the residue distilled in vacuum. A fraction boiling at 212-213° (1 mm) was collected. Yield 11.5 g (59%).

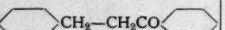
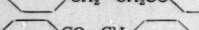
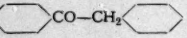
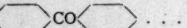
* This reaction can be carried out in an aqueous medium in the absence of alcohol without lowering the yield, but the quality is reduced.

TABLE 1

Ketones of the General Formula RO 

Substance number	R	Yield (%)	Melting or boiling point	Found (%)			Calculated (%)			Melting point of citrate	Epitheliating action	Toxicity
				C	H	N	C	H	N			
(II)	CH_3	72.4	96—96.5°	—	—	—	—	—	—	—	Active for 15 days	Not toxic
(III)	C_2H_5	80.5	205 (1 мм)	80.58	7.26	—	80.50	7.10	—	—	Active for 220-27 days	
(IV)	$(C_2H_5)_2N-CH_2-CH_2$	59	212—213 (1 мм)	76.96	8.29	4.36	77.5	8.31	4.31	118—119[c]	Not determined	Highly toxic
(V)	$(CH_3)_2N-CH_2-CH_2-CH_2$	40	238—240 (1 мм)	76.85	8.00	4.15	77.4	8.26	4.51	124—12	Active but weaker than (II) or (III)	Not toxic

TABLE 2

Substance number	Ketones	Yield (%)	Boiling point	Found (%)			Calculated (%)			Melting point of citrate	Epitheliating action	Toxicity
				C	H	N	C	H	N			
(VII)	RO• 	41.5	242—244° (3 мм)	77.75	8.47	4.15	77.50	8.31	4.31	116—117°	Inactive	Nontoxic
(VIII)	RO 	58	195—200 (3 мм)	78.36	8.09	4.55	77.4	8.05	4.50	112—114	Weakly active	
(IX)	RO 	42.1	230 (3 мм)	75.85	7.98	5.05	75.95	8.08	4.91	138	Highly active for 7-8 days	
(X)	RO 	58.5	180 (1 мм)	71.74	9.12	6.33	71.5	8.96	5.98	119—120	Weakly active	

• R = $(C_2H_5)_2NCH_2CH_2$.

The citrate of this substance was obtained from the ketone base and citric acid in alcoholic solution; yield 78%, m.p. 118-119°.

Compounds V, VII-X were prepared under similar conditions.

SUMMARY

1. A simple method was developed for the preparation of p-hydroxyphenyl-phenethyl ketone – a compound unknown up to now.

2. Simple methods were developed for the preparation of various ethers of p-hydroxyphenyl-phenethyl ketone.

3. Some of the members of the group of preparations of ethers of p-hydroxy-fatty-aromatic- and aromatic ketones proved to be active as epitheliating agents.

LITERATURE CITED

[1] P. Pfeiffer, J. prakt. Chem. 108, 347 (1924).

[2] American Patent No. 2668850 (1954); C. A. 49, 32521 (1955).

[3] N. Wilson et al., J. Invest. Dermatol. 21, 3 (1953).

[4] R. Shriner and T. Kurosava, J. Am. Chem. Soc. 52, 2538 (1930).

[5] W. Schneidewind, Ber. 21, 1323 (1888).

[6] F. Dippy and R. Lewis, Record (Wash., D. C.) 56, 1004 (1937).

[7] F. Straus and H. Grindel, Ann. 439, 276 (1924).

[8] S. Weisl, Monatsh. 26, 977 (1905).

[9] K. Rosemund and W. Schnurr, Ann. 460, 89 (1928).

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SYNTHESES OF ORGANOSILICON COMPOUNDS

I. THE MECHANISM OF THE REACTION BETWEEN METHYL CHLORIDE AND SILICON IN PRESENCE OF COPPER

A. L. Klebansky and V. S. Fikhtengolts

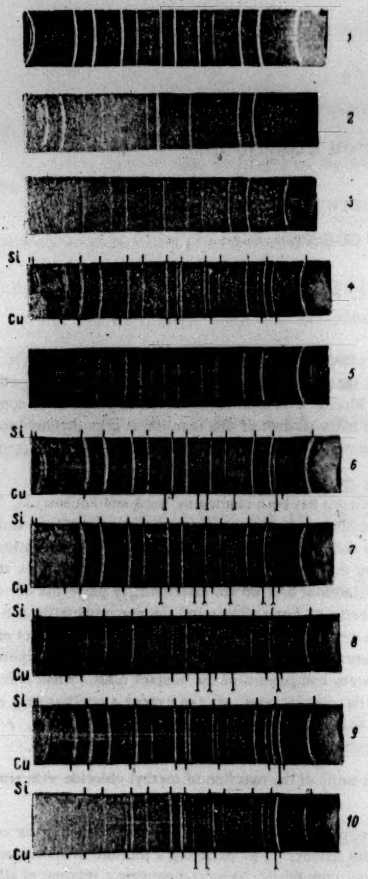
Among the great diversity of organosilicon compounds, considerable theoretical and practical interest is attached to the methylchlorosilanes and their derivatives – the methylpolysiloxanes. The most convenient synthesis of methylchlorosilanes is Rochow's reaction [1] of methyl chloride with elemental silicon in presence of copper as catalyst which lowers the temperature of the reaction. The main product of this reaction is dimethyldichlorosilane $(CH_3)_2SiCl_2$. It is accompanied by a series of other substances: CH_3SiCl_3, $(CH_3)_3SiCl$ and CH_3SiHCl_2. Carbon, hydrogen, methane, etc. are also found.

The mechanism of the direct synthesis of methylchlorosilanes has been studied by Hurd and Rochow [2]. The authors put forward the theory that methyl chloride and copper interact at the interface between the silicon and the copper to form the unstable and volatile compound CH_3Cu and copper chloride. The latter reacts with silicon to form an active intermediate compound [SiCl] which links up in diverse ways with CH_3Cu and CuCl to give the great variety of products mentioned above. The author's experimental data do not convincingly prove the correctness of their proposed mechanism which is based on reactions between free radicals and the organometallic compound CH_3Cu. The theory is at variance with the authors' own observations of the inability of silicon to react either with free radicals or with copper alkyls. In our opinion the contradictions stem from the fact that all the experimental evidence is based on experiments carried out with separate components of the contact mass. When both components are present under the conditions of preparation of the contact mass, we can expect a qualitatively different state of the silicon and the copper, and the mechanism will then have an entirely different character. A rather different mechanism of this reaction, not based on experiment, was advanced by K. A. Andrianov [3].

The foregoing considerations prompted us to undertake a study of the reaction of methyl chloride with silicon in presence of copper.

Structure of the contact mass and the catalytic role of copper. Contacting of silicon with copper in our contact mass was effected in various ways: 1) by fusing copper with silicon; 2) by pelleting a mixture of silicon and copper powders followed by sintering of the pellets in a hydrogen atmosphere; 3) by compacting a mixture of silicon and copper chloride powders, distilling off the $SiCl_4$ by heating, and depositing metallic copper on silicon.

X-ray examination of the contact mass established that an intermetallic compound of silicon and copper is formed under the conditions of their preparation and this compound participates in the process of formation of methylchlorosilanes. Each of the substances used for preparation of the contact mass possesses its own characteristic distribution of lines in the x-ray spectrum (see diagram, roentgenograms 1-3). The same lines of the original substances are detected in the diagrams (4-5) after pelleting of the contact mass. After suitable thermal treatment, these contact masses become active and new lines are observed on their roentgenograms (6-8). The latter are designated by the symbol A. They testify to the formation of a new phase with a specific type of crystal lattice. The copper lines are considerably weakened on these roentgenograms. Since we know that fusion of silicon with copper leads to formation of their intermetallic compound, the appearance of fresh lines on the roentgenogram of the melt (6) must be attributed to the formation of this compound. A similar distribution of lines on the roentgenograms of contact masses of other types (7 and 8) testifies to the formation of the same intermetallic compound under the conditions of their preparation. Roentgenogram 9, obtained with a specimen of contact mass taken during preparation of methylchlorosilanes, contains somewhat weaker lines of intermetallic compound and stronger copper lines. This



Roentgenograms of contact masses and of the components used in their preparation. 1) Silicon, 2) copper, 3) cuprous chloride, 4) unsintered contact mass of silicon and copper powders, 5) pellet of silicon and cuprous chloride, 6) melt of silicon with copper, 7) sintered contact mass from silicon and copper powders, 8) contact mass containing chemically precipitated copper, 9) partially spent contact mass, 10) completely spent contact mass.

TABLE 1

Influence of the Structure of the Organic Radical of the Alkyl Chloride on the Temperature of Reaction of the Latter with Silicon.

Formula of alkyl chloride	Dipole moment (D)	Temperature of reaction with silicon	
		in absence of copper	in presence of copper
CH_3Cl	1.92	370—380°	280—300°
CH_3CH_2Cl . .	2.05	310—320	190—200
$(CH_3)_2CHCl$ . .	2.15	About 220	110—120
$(CH_3)_3CCl$ . .	2.13	—	120—125

TABLE 2

Influence of the Structure of the Organic Radical of Chloro Compounds on the Temperature of Their Reaction with Silicon (in presence of copper).

Formula of compound	Temperature of reaction with silicon
CH_3Cl	300—320°
$CH_2=CH-CH_2Cl$ . .	200—210
$CH_3-CCl=CH-CH_2Cl$	Below 150

is a basis for assuming that copper is regenerated from the intermetallic compound participating in the formation of methylchlorosilanes. This regenerated copper again forms an intermetallic compound with the silicon present in excess, as is confirmed by the presence of the lines of the intermetallic compound on the diagram of the fully spent contact mass (10). The intermetallic compound evidently exists in dynamic equilibrium with the pure components when the contact mass is in use.

We propose the following mechanism of the catalytic action of copper: Under the influence of the ionic charges of the crystal lattice of the intermetallic compound, the polar molecules of methyl chloride absorbed on the surface of the contact mass undergo further polarization and deformation of the C—Cl bond. Due to this, the stability and energy of dissociation of this bond are lowered, and this is reflected in a lowering of the temperature of reaction with silicon. In the alkyl chloride series an increase in the degree of polarization of the C—Cl bond should be observed with progressive substitution of the hydrogens of methyl chloride by methyl groups, due to the displacement of the electronic density to the halogen atom:

$$\overset{+}{C}H_3\overset{\frown}{-}\overset{-}{Cl} < CH_3\rightarrow\overset{+}{C}H_2\overset{\frown}{-}\overset{-}{Cl} < \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\overset{+}{C}H\overset{\frown}{-}\overset{-}{Cl} < \begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!\!>\overset{+}{C}\overset{\frown}{-}\overset{-}{Cl}.$$

This is confirmed by the magnitudes of the dipole moments (Table 1) obtained from the velocities of hydrolysis of alkyl halides [4] and by the increased electrical conductivity of the organic radicals of the corresponding alkyl chlorides which was established by Kharasch and other workers [5]. Consequently, if, as we suggest, the temperature of reaction of alkyl chlorides with silicon depends upon the polarity of the C–Cl bond, then in this series we should expect a lowering of the reaction temperature, independent of the presence of copper. The experimental data fully confirmed this hypothesis (Table 1).

Intensification of the ionization and, in turn, of the reactivity of the chlorine atom in allyl chloride in comparison with methyl chloride takes place under the polarizing influence of the double bond conjugated with the C–Cl bond:

$$CH_2=\overset{\frown}{C}H\rightarrow\overset{+}{C}H_2\overset{\frown}{-}\overset{-}{Cl}$$

The C–Cl bond is even more strongly ionized in 2,4-dichlorobutene-2 in which the polarizing effect of the double bond is intensified by the conjugation of the ungeneralized pair of electrons of the chlorine atom in the 2-position with the π-electrons of the double bond. This is confirmed by the increased reactivity of dichlorobutene in comparison with that of allyl chloride. Thus, the rate of saponification of 2,4-dichlorobutene-2 by sodium ethoxide at 50° is 5-6 times greater, and the velocity of exchange with KI in acetone is 23-28 times greater than for allyl chloride [6]. These properties are reflected in the temperature of reaction of these compounds with silicon (Table 2).

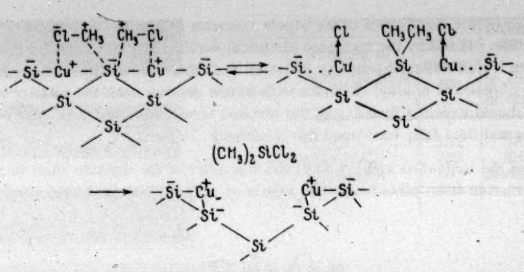
We observed the opposite effect in the case of chlorobenzene and vinyl chloride where, as a result of the displacement of the electronic density (ungeneralized electron pair) of the chlorine atom to the double bond under the influence of conjugation, the polarizability of the C–Cl bond is lowered. Both of these compounds only react to a slight extent with silicon in presence of copper and at a temperature higher than 400° [7].

All that has been said above confirms the dependence of the temperature of reaction of alkyl chlorides with silicon on the polarizability of the C–Cl bond. Consequently, the lowering of the temperature of reaction of each alkyl chloride due to the presence of copper (Table 1) may be analogy also be explained by the increased polarizability of the C–Cl bond (by lowering of its dissociation energy) under the influence of the ionic charges of the crystal lattice of the intermetallic compound. In the absence of copper the dissociation of the C–Cl bond takes place only under the influence of thermal action.

Mechanism of formation of methylchlorosilanes. Interaction of methyl chloride with the silicon of the contact mass gives a mixture of methylchlorosilanes $(CH_3)_2SiCl_2$, CH_3SiCl_3, $(CH_3)_3SiCl$ and CH_3SiHCl_2 and products of pyrolysis C, CH_4, $CH_2{=}{=}CH_2$ and H_2. The composition and yields of individual products vary with the conditions of the reaction.

We propose the following mechanism of formation of the foregoing products of reaction: The methyl chloride is chemisorbed on the surface of the intermetallic compound with consequent lowering of the energy of dissociation of the C–Cl bond, and this is accompanied by a lowering of the reaction temperature. It may be suggested that dissociation of the methyl chloride will, under the influence of the charges of the atoms of the crystal lattice of the intermetallic compound, be followed by addition of methyl groups to silicon atoms and of chlorine atoms to copper. In the latter case, however, we suggest, contrary to the view of Hurd and Rochow, that cuprous chloride will not be formed. We base our disagreement on the fact that cuprous chloride does not react with silicon until a temperature of 260° is reached, and consequently we should not expect the formation of alkylchlorosilanes at below this temperature. Moreover, the formation of some alkylchlorosilanes, as we have shown, is already observed at 110-125° (Table 1). Consequently, while not denying the role of copper as a carrier of the chlorine atom from methyl chloride to silicon, we suggest that the copper atom, while binding the chlorine atom, remains bound to some extent to the crystal lattice of the intermetallic compound. The Cu–Cl bond in this complex will be polarized under the influence of the charges of the crystal lattice and will therefore be more reactive than in cuprous chloride where it has mainly a covalent character.

Subsequently the formation of dimethyldichlorosilane takes place due to transfer of the chlorine atoms from the above mentioned complex to the neighboring atom of silicon which is linked to methyl groups. In this process the intermetallic compound is regenerated:



The following mechanism of formation of methyltrichlorosilane under the same conditions may be proposed: some of the methyl groups, which are formed by dissociation of methyl chloride and which addon to silicon atoms (and which in some cases donot add on) undergo thermal breakdown with formation of carbon and gaseous decomposition products. The chlorine atoms combined with the copper atoms of the intermetallic compound are present in excess over the methyl groups which have not decomposed and which are bound to silicon. This would account for the formation on certain parts of the contact mass of methyltrichlorosilane, as well as of $SiCl_4$ under very drastic temperature conditions.

On the basis of our analytical data, the formation of methyltrichlorosilane may be represented by the following equations:

$$Si + 3CH_3Cl \begin{cases} \nearrow CH_3SiCl_3 + CH_4 + C + 2H \ (\rightarrow H_2) \\ \searrow CH_3SiCl_3 + CH_2 = CH_2 + 2H \ (\rightarrow H_2), \end{cases}$$

the first reaction being the dominating one and constituting 85-90% of the conversion. These equations are fully in harmony with the fact that with rising temperature there is a consistent increase in yield of methyltrichlorosilane as well as of gaseous products of decomposition. This increase is matched by a corresponding decrease in yield of dimethyldichlorosilane.

TABLE 3

Influence of Donors and Acceptors of Chlorine on the Yield of Methyltrichlorosilane.

HCl and CH_3Cl added (%)	Mg added to contact mass (%)	Yield of CH_3SiCl_3 on CH_3Cl reacted (in % of theoretical)
–	–	41
38.5	–	86
–	5	31
–	10	21

TABLE 4

Decomposition of Methyl Chloride over Copper

Temperature	Methyl chloride decomposed	
	from data of gas analysis (%)	from sum of chlorine in CuCl and HCl (in %)
350°	1.6	–
400	3.3	3.25
450	35.1	34.1

Confirmations of the probability of the above mechanism of formation of methyltrichlorosilane were obtained experimentally. In the synthesis of methylchlorosilanes in presence of hydrogen chloride, which we found

to relatively easily donate chlorine atoms to the silicon of the contact mass, the yield of methyltrichlorosilane rises sharply. Conversely, on introducing magnesium powder, which enters into firm combination with chlorine, the yield of methyltrichlorosilane is sharply reduced (Table 3).

There is therefore no doubt about the relation between the yield of methyltrichlorosilane and the ratio of methyl groups to chlorine atoms.

As indicated above, the cause of the change of this ratio and of the formation of gaseous products of decomposition is the pyrolysis of the methyl groups of the dissociating methyl chloride. Confirmation of this was obtained by passing methyl chloride over heated copper powder which had been reduced by hydrogen, when dissociated of methyl chloride and addition of chlorine atoms to copper was observed. The free methyl radicals then underwent thermal rearrangement with formation of carbon and of gaseous decomposition products whose composition was similar to that in the synthesis of methylchlorosilanes. The yield of decomposition products was insignificant at 350°, i.e. at a temperature somewhat higher than that at which methyl chloride usually interacts with the contact mass, and increased sharply at above 400°, i.e. at the very temperatures at which methyl chloride reacts with silicon in the absence of copper, due to thermal dissociation of methyl chloride (Table 4). It must be noted that at the same time cuprous chloride is partly reduced by atomic hydrogen (originating from pyrolysis of methyl groups) with formation of hydrogen chloride. According to the analytical data, the amount of gaseous products of decomposition of methyl chloride corresponds to the amount of CuCl and HCl formed.

It may be suggested that the formation of hydrogen-containing compounds CH_3SiHCl_2 and CH_3SiH_2Cl (traces of the second) is the result of hydrogenation of silicon atoms of the intermetallic compound by atomic hydrogen formed by decomposition of methyl groups. This hypothesis is confirmed by the following facts. On replacing the methyl radical by ethyl (which has a lower thermal stability), the yield of hydrogen-containing compounds is several times larger and reaches 30-50%. Hydrogenation of silicon is also observed on passing hydrogen chloride over the contact mass, considerable amounts of $HSiCl_3$ and H_2SiCl_2 being formed together with $SiCl_4$.

Formation of trimethylchlorosilane may be regarded as the result of a characteristic disproportionation reaction taking place during formation of the products of the reaction at the active surface of the intermetallic compound:

$$4CH_3Cl+2Si \longrightarrow CH_3SiCl_3+(CH_3)_3SiCl.$$

The theoretically possible reaction

$$2(CH_3)_2SiCl_2 \rightleftharpoons CH_3SiCl_3+(CH_3)_3SiCl$$

is excluded because it was experimentally established that dimethyldichlorosilane is a stable product under the conditions of the process and does not undergo any transformations.

Consequently, contrary to the theory of Hurd and Rochow of a multistage radical mechanism, we advance an experimentally founded contact-catalytic mechanism of a process proceeding at the surface of the ionized intermetallic compound of silicon and copper.

It is our pleasant duty to convey thanks to D. I. Dobychina and A. M. Zagrubsky for carrying out the x-ray analysis and for assistance in the interpretation of the analytical results.

SUMMARY

1. It was established with the help of x-ray analysis that, under the conditions of preparation of various types of contact masses, an intermetallic compound of silicon and copper is formed which is responsible for the catalytic activity of contact masses.

2. Theoretical and experimental evidence was advanced for the existence of a relation between the polarity of the C–Cl bond of an alkyl chloride and the temperature of its interaction with silicon. The catalytic role of copper, manifested in the lowering of the temperature of reaction of alkyl chloride with silicon, is explained by the increased polarity of the C–Cl bond under the influence of the ionic charges of the crystal lattice of the intermetallic compound.

3. A mechanism of formation of a series of methylchlorosilanes with participation of the intermetallic compound is advanced. The role of copper as a carrier of chlorine atoms from methyl chloride to silicon is demonstrated.

4. Experimental proof is adduced for a mechanism of formation of methyltrichlorosilane and hydrogen-containing compounds as a result of pyrolysis of methyl radicals at the surface of the contact mass.

LITERATURE CITED

[1] E. G. Rochow, J. Am. Chem. Soc. 67, 963 (1945).

[2] D. T. Hurd and E. G. Rochow, J. Am. Chem. Soc. 67, 1057 (1945).

[3] K. A. Andrianov, A. A. Zhandov, S. A. Golubtsov, and M. V. Sobolevsky, Progr. Chem. 18, 145 (1949).

[4] A. E. Remick, Electronic Interpretations of Organic Chemistry (Foreign Lit. Press, Moscow, 1950), 135 et seq.

[5] M. S. Kharasch and A. L. Flenner, J. Am. Chem. Soc. 54, 681 (1932); F. C. Whitmore and H. Bernstein, J. Am. Chem. Soc. 60, 2626 (1938).

[6] L. F. Hatch and S. G. Ballin, J. Am. Chem. Soc. 71, 1041 (1949).

[7] E. G. Rochow and W. F. Gilliam, J. Am. Chem. Soc. 67, 1772 (1945); D. T. Hurd, J. Am. Chem. Soc. 67, 1813 (1945).

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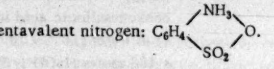
ABSORPTION SPECTRA AND STRUCTURE OF BENZENE DERIVATIVES

XX. SPECTROGRAPHIC INVESTIGATION OF p-AMINOBENZENESULFONIC ACID AND ITS DERIVATIVES

N.A. Valyashko* and N.P. Romazanovich

Previous studies were devoted to the spectrographic examination of conjugation of the benzene ring with the chromophoric carbonyl group and the auxochromic hydroxyl group. In the present work we studied the conjugation of the strongly auxochromic amino group with the benzene ring and with the chromophoric sulfonic group which lacks neutral double bonds. The compounds studied in this connection were p-aminobenzenesulfonic acid and its derivatives. The acid is an important substance because in the form of the amide, known in the USSR as white streptocide [1], it possesses valuable chemotherapeutic properties and serves as starting compound for many important medicinals [2].

Spectrographic investigation of p-aminobenzene sulfonic acid. It was long ago suggested that p-aminobenzenesulfonic acid exists in the form of an inner salt [3].

On the basis of the properties of the acid, B.N. Menshutkin [4] proposed a formula without a free amino group and with pentavalent nitrogen:  .

This theory was accepted by A.E. Chichibabin [5] and by the authors of other textbooks of organic chemistry [6-8]. In 1923 Bjerrum [9], on the basis of recalculation of the dissociation constants, arrived at the conclusion that p-aminobenzenesulfonic acid exists exclusively in the form of the dipole ion $H_3\overset{+}{N}-C_6H_4-SO_3^-$. Sidgwick [10] and L. and M. Fieser [11] also assume the formula of a dipolar ion for the acid. In these formulas the conjugation of the amino and sulfo groups with the benzene ring is ignored.

The absorption spectra of p-aminobenzenesulfonic acid were investigated by Pestemer and Flaschka [12] and by Böhme and Wagner [13]. The latter noted the inconsistency of a dipolar character of the acid with the results of spectrographic investigations, but they drew no conclusions about the structure of the acid. Grammaticakis [14] studied the absorption spectra of p-aminobenzenesulfonic acid in water and in sodium hydroxide and pointed out that it can exist not only in the form of the dipolar ion $H_2\overset{+}{N}-C_6H_4-SO_3^-$, as was generally assumed in recent times, but also in the form of the amino acid $H_2N-C_6H_4-SO_3H$.

We investigated the absorption spectra of p-aminobenzenesulfonic acid at concentrations of 10^{-1} to 10^{-5} M in water, in 40% ethanol, in solutions of sodium hydroxide of various strengths and in 1 N hydrochloric acid. Comparison of the absorption spectrum of the aqueous solution of p-aminobenzenesulfonic acid with the spectrum of benzenesulfonic acid [15] and aniline shows that introduction of an amino group in the para position to the sulfonic group leads to conjugation of these groups with the benzene ring, with development of the absorption bands typical of para derivatives (Fig. 1, curves 1-3). Such a band, as shown earlier by N.A. Valyashko [16] and Valyashko and Rozum [17], is an offshoot of the φ band of the original compound, in the present case the φ band of benzenesulfonic acid. The absorption maximum of p-aminobenzenesulfonic acid at λ 2940 A and ϵ 16600 is here shifted to the extent of 170 A into the short-wave region, and the absorption intensity becomes 23 times greater than that of the φ band of benzenesulfonic acid. The long-wave edge of the absorption band of p-aminobenzenesulfonic acid runs parallel to that of the first absorption band of aniline. It is possible that the presence of this band causes an inflection of the absorption curve of p-aminobenzenesulfonic acid at λ 3025-2780 A and ϵ 400-1800.

* Deceased.

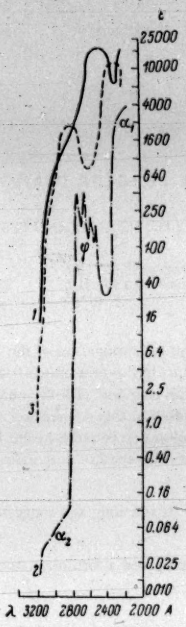


Fig. 1. Comparison of absorption spectra of p-aminobenzenesulfonic acid, aniline and benzenesulfonic acid.
1) aminobenzenesulfonic acid in water (10^{-2} - 10^{-4} M); 2) benzenesulfonic acid in water (6.5, 6.5 . 10^{-1} - 6.5 . 10^{-4} M); 3) aniline in water (10^{-1} - 10^{-4} M).

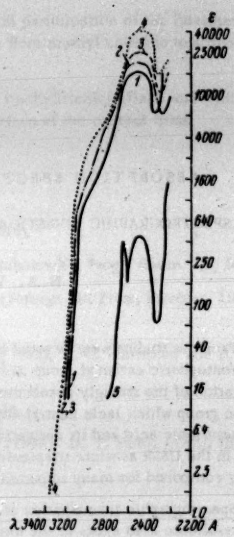


Fig. 2. Absorption spectra p-aminobenzenesulfonic acid in various solvents. 1) in water (10^{-2} - 10^{-4} M), 2) in water + 100 moles NaOH, 3) in 1 N NaOH (10^{-2} - 10^{-5} M), 4) in 3 N NaOH (10^{-1} - 10^{-5} M), 5) in 1 N HCl (10^{-2} - 10^{-3} M).

In alkali solution p-aminobenzenesulfonic acid should not contain the $\overset{+}{N}H_3$ group because the $\ddot{N}H_2$ group is formed by the action of the hydroxyl ion.

$$H_3\overset{+}{N}-C_6H_4-SO_3^- + OH^- \longrightarrow H_2\ddot{N}-C_6H_4-SO_3^- + H_2O.$$

However, the character of the absorption of p-aminobenzenesulfonic acid does not change under the influence of sodium hydroxide solutions. The position of the maximum remains at λ 2490 A. With increasing concentration of alkali only the intensity of the absorption band changes by factors of 1.2, 1.5 and 2.4 in comparison with the maximum in water (Fig. 2, curves 1-4).

The action of 1 N solution of hydrochloric acid on p-aminobenzenesulfonic acid consists in the formation of a salt at the amino group, a proton adding on to the unshared electron pair of nitrogen with formation of the NH_3 group. This is expressed spectrographically by a sharp change in the absorption spectrum of p-aminobenzenesulfonic acid, since the conjugation of the amino group with the benzene ring is nearly completely surpressed. The absorption intensity decreases by a factor of 33, and the absorption band becomes similar to the φ band of benzenesulfonic acid but differ from it in that the second, third, and fourth narrow bands of benzenesulfonic acid are replaced by one broad band at λ 2560 A and ε 500; the maximum of the narrow band lies at λ 2690 A and ε 400.

Investigation of the electrical conductivity of p-aminobenzenesulfonic acid. A physicochemical study was made of the binary system p-aminobenzenesulfonic acid-sodium hydroxide by the method of N.S. Kurnakov [18].

Solutions of 0.01 N p-aminobenzenesulfonic acid and 0.01 N sodium hydroxide in 40 % ethanol were prepared. Platinum electrodes were used. The over-all concentration of the solutions was 0.02 M. Measurements were made at 24°.

The electrical conductivity was plotted on the ordinates and the number of moles of p-aminobenzenesulfonic acid and alkali or hydrochloric acid in solution was plotted on the abscissas. A special singular point (a minimum) on the composition/electrical-conductivity curve (Fig.3, curve 1) at 1:1 ratio of components testifies to the formation of a new chemical compound – the sodium salt of p-aminobenzenesulfonic acid. The instant of neutralization is characterized by a minimum of electrical conductivity when highly conductive ions of hydrogen and hydroxyl are no longer present in solution.

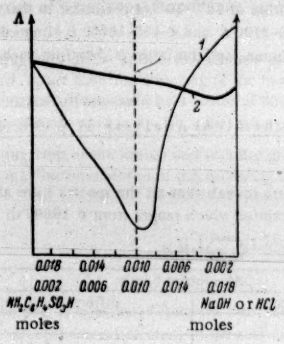


Fig. 3. Composition/electrical conductivity diagram in the binary systems: p-aminobenzenesulfonic acid-sodium hydroxide, p-aminobenzenesulfonic acid-hydrochloric acid at 24°.

Conductometric titration of p-aminobenzenesulfonic acid was also carried out and confirmed the ocurrence of the equivalent point at a 1:1 molar ratio of p-amino-benzenesulfonic acid to alkali.

The electrical conductivity in the binary system p-aminobenzenesulfonic acid-hydrochloric acid was measured in the same manner as in the system p-amino-benzenesulfonic acid-sodium hydroxide. The curve (Fig. 3, curve 2) shows that at the start the electrical conductivity of the solution does not alter with rising concentration of HCl; later it falls and reaches a minimum at a 1:9 molar ratio of components. Such a large excess of HCl over p-aminobenzenesulfonic acid at the equivalent point is the result of the basicity of the amino group in the p-aminobenzenesulfonic acid being weakened by conjugation with the sulfo group.

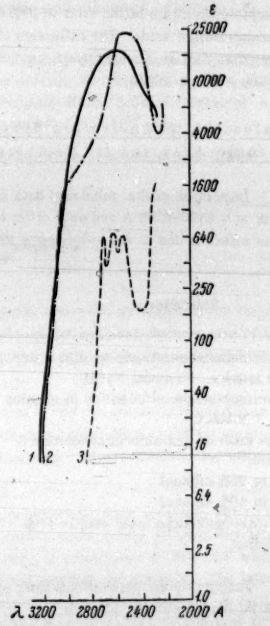


Fig. 4. Absorption spectra of p-aminobenzenesulfonamide in various solvents. 1) in water ($10^{-2} - 10^{-4}$ M); 2) in 1 N NaOH ($10^{-2} - 10^{-5}$ M), 3) in 1 N HCl ($10^{-2} - 10^{-3}$ M).

Detailed spectrographic investigation of p-aminobenzenesulfonic acid and the examination of the electrical conductivity of its solutions both indicate that p-aminobenzenesulfonic acid does not possess the structure of an inner salt or a dipolar ion.

Spectrographic investigation of p-aminobenzenesulfonamide and the ethyl ester of p-aminobenzenesulfonic acid. The absorption spectrum of p-aminobenzenesulfonamide in water at a concentration of $10^{-2} - 10^{-4}$ M (Fig. 4, curve 1) is similar to the absorption spectrum of p-aminobenzenesulfonic acid in water; the only

difference is that the inflection of the curve observed in the spectrum of the acid is lowered and runs together with the φ band into a broad band with a mixmum at λ = 2560 A and ϵ 16600. This inflection appears in the absorption spectrum of alkaline solutions (Fig. 4, curve 2).

Hydrochloric acid has the same influence on the absorption spectrum of p-aminobenzenesulfonamide that it has on the spectrum of p-aminobenzenesulfonic acid. The intensity of the absorption band of the aqueous solution of p-aminobenzenesulfonamide in the acid is lowered by a factor of 22. The mean maximum of the absorption band, which is split up into three narrow bands, lies at λ 2620 A and ϵ 700 (Fig. 4, curve 3), and approximates to the absorption spectrum of benzenesulfonamide in water [15]. Our experimental results were similar to those of Kumler and Streit [19].

The ethyl ester of p-aminobenzenesulfonic acid was obtained by the literature method [20-22]. The absorption spectrum of the ester in 95% ethanol at a concentration of 10^{-2}-10^{-4} M is similar to that of p-aminobenzenesulfonic acid. The inflection of the curve at λ 3100-2700 A and ϵ 400-10000 is situated very much lower than that of the acid itself, but does not reach the maximum, and the latter is therefore unchanged at λ 2500 A and ϵ 16600.

Evaluation of Absorption Spectra and Physicochemical Analysis of p-Aminobenzenesulfonic Acid and Its Derivatives

Inspection of the tabulated data for the absorption spectra reveals that all the spectra have absorption bands at λ 2490-2500 A and only differ in the intensity of absorption which ranges from ϵ 16600 to 2400. The latter effect is due to the influence of the solvent.

Substance	Absorption bands			
	maximum		inflection of curve	
	λ	ϵ	λ	ϵ
p-Aminobenzenesulfonic acid in water	2490	16600	3025-2780	400-1800
The same + 100 moles NaOH	2490	20000	3055-2750	500-3600
p-Aminobenzenesulfonamide in solution in 1 N NaOH	2490	24000	3040-2770	1000-4000
Ethyl ester of p-aminobenzenesulfonic acid:				
in 95% ethanol	2500	16600	3100-2700	4000-10000
in 40% ethanol	2500	16600		
p-Aminobenzenesulfonic acid in 40% ethanol	2500	16600	3120-2900	50-360

Judging by the general character of the absorption spectra, the structure of the compounds investigated must be fundamentally the same.

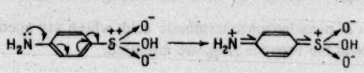
The molecule of p-aminobenzenesulfonic acid in sodium hydroxide solution contains the NH_2 group; the ethyl ester of p-aminobenzenesulfonic acid can likewise not contain the NH_3 group because the hydrogen of the sulfo group is substituted. The identity between the absorption spectra of these substances and the absorption spectrum of an aqueous solution of p-aminobenzenesulfonic acid indicates that its molecule likewise contains the NH_2 group. This conclusion is in harmony with the results of measurement of the electrical conductivity of ethanol solutions of p-aminobenzenesulfonic acid with sodium hydroxide and hydrochloric acid. A dipolar ion would have required a larger amount of alkali since a portion of the hydroxyl ions would have been consumed in the separation of a proton from the NH_3 group. With hydrochloric acid the instant of formation of salt is accompanied by transition of the NH_2 to the NH_3 group, and this results in a special point (a minimum).

The correctness of our conclusion about the structure of the p-aminobenzenesulfonic acid molecule is confirmed by data for the heat of neutralization. According to Devotc [23], a characteristic of dipolar ions is a low heat of neturalization. The heat of neutralization of acids is due mainly to the reaction of formation of water. The neutralization of dipolar ions, however, involves the dissociation $\overset{+}{N}H_3 \rightarrow NH_2 + H^+$, an

endothermic process accompanied by great absorption of heat. The heat of neutralization of aminoacetic acid (2.9 kcal) is therefore 10 kcal less than that of acetic acid (13.29 kcal) [24]. The heat of neutralization of p-aminobenzenesulfonic acid, according to Massol [25], is +9.07 kcal; a value of + 10.45 kcal was later found by Swientoslawski [26] in presence of sodium hydroxide. Devoto [24] obtained a value of 9.7 kcal. Massol compared the heats of neutralization (in kcal) of sulfurous, phenylsulfurous and aminophenylsulfurous acids in order to show the successive influence of the C_6H_5 and NH_2 groups in weakening the acidity of sulfurous acid: sulfurous acid, freshly dissolved, 16.6, phenylsulfurous acid 13.6, p-aminophenylsulfurous acid 9.07. The influence of the aromatic nucleus is reflected in a lowering of the heat of neutralization of sulfurous acid by 3 kcal, while the introduction of an amino group in the para position of the benzene ring causes a further drop of 4.53 kcal. The lowering of the heat of neutralization is caused by the conjugation of the sulfonic group with the benzene ring and of the p-amino group with the benzene ring and the sulfonic group. The heat of neutralization of p-aminobenzenesulfonic acid likewise does not provide confirmation of its structure as a dipolar ion.

Conjugation of the amino and sulfonic groups with the benzene ring in p-aminobenzenesulfonic acid is expressed, apart from the lowering of the heat of neutralization, by lowering of the ionization constant of p-aminobenzenesulfonic acid by a factor of 330 in comparison with benzenesulfonic acid: the value of K_{25} for benzenesulfonic acid is $2 \cdot 10^{-1}$, that for p-aminobenzenesulfonic acid is $6.05 \cdot 10^{-4}$ [27].

Conjugation of the amino and sulfonic groups with the benzene ring in the p-aminobenzenesulfonic acid molecule may be represented in the following manner:



An electron pair is transferred from the benzene ring to the sulfonic group under the influence of the large positive charge of the sulfur atom of the sulfonic group, and the transfer of the unshared electron pair of the nitrogen from the amino group to the benzene ring is intensified to give a stable conjugated system of amino and sulfonic groups with the benzene ring.

Consequently, our spectrographic investigations and measurements of the electrical conductivity in alkali and acid solutions, as well as the heat of neturalization of p-aminobenzenesulfonic acid (as determined by Massol and others), do not confirm Bjerrum's conclusion [9] of the existence of p-aminobenzenesulfonic acid exclusively in the form of dipolar ions.

As our studies show, the amino and the sulfonic group in p-aminobenzenesulfonic acid are, due to the conjugation with the benzene ring, respectively a weakly basic and weakly acidic group. p-Aminobenzenesulfonic acid is insoluble in alcohol, ether and benzene but dissolves in hot water; it decomposes at 280-300° without melting. These properties are in sharp contrast with those of aniline and benzenesulfonic acid. The latter is readily soluble in water, melts at 50° and can be distilled without decomposition in high vacuum. p-Aminobenzenesulfonic acid dissolves in aqueous solutions of caustic alkalies, but is not reactive with mineral acids although it contains an amino group. The sodium salt of p-aminobenzenesulfonic acid may be acetylated to an N-acetyl compound, but the free acid does not acetylate. According to Sidgwick [10] this is an indication that the salt, but not the acid, contains the NH_2 group. In the light of our investigations another explanation of these properties is forthcoming.

The ethyl ester of p-aminobenzenesulfonic acid that we investigated is a white, bulky crystalline powder with m.p. 82° readily soluble in ethanol and ether but insoluble in water. After standing for a week, this ester changes its solubility, and the crystals melt at 255°. The absorption spectra of p-aminobenzenesulfonic acid and its ester are very similar and indicate an identical structure. The low melting point of the ethyl ester of p-aminobenzenesulfonic acid is evidence that the high-melting p-aminobenzenesulfonic acid is strongly associated. The sulfonic group promotes solubility. This property may be associated with the tendency of the sulfonic group to form hydrogen bonds. In the ester the hydrogen is substituted at the ethyl and the ester is therefore insoluble in water.

Since the NH_2 group has already donated an unshared electron pair on conjugation with the benzene ring, it will finally manifest inertness to the action of mineral acids, but at the same time it loses the ability to

form a salt with excess of acid, as evidenced by the absorption spectra and the values of the electrical conductivity of solutions of p-aminobenzenesulfonic acid containing HCl.

During formation of a salt with alkali metals, p-aminobenzenesulfonic acid changes into an anion in which the increase in the negative charge of the oxygen will partly lower the positive charge of the sulfur atom, thereby weakening the bond of the free electron pair of nitrogen with the benzene ring and thus endowing it with the ability to enter into the acetylation reaction.

The properties of p-aminobenzenesulfonic acid that served as a basis for the hypothesis of its existence in the form of an inner salt or a dipolar ion are fully consistent with the concept of conjugation of the amino and sulfonic groups with the benzene ring in the molecule of p-aminobenzenesulfonic acid.

SUMMARY

1. The absorption spectra of p-aminobenzenesulfonic acid and p-aminobenzenesulfonamide were investigated in water and in solutions of sodium hydroxide and hydrochloric acid; the spectra of the ethyl ester of p-aminobenzenesulfonic acid were examined in 95 and 40% ethanol; p-aminobenzenesulfonic acid was also examined in 40% ethanol.

2. The absorption spectrum of p-aminobenzenesulfonic acid contains a strong band characteristic of benzene derivatives containing an auxochromic and chromophoric group in the para position (in the present case the amino and the sulfonic group). These groups enter into conjugation with the benzene ring.

3. The special properties of p-aminobenzenesulfonic acid, which are accounted for by conjugation of the amino and sulfonic group with the benzene ring, are discussed.

4. Measurements were made of the electrical conductivity of the binary systems p-aminobenzenesulfonic acid–sodium hydroxide and p-aminobenzenesulfonic acid–hydrochloric acid in dependence on the ratio of components.

5 The existence of p-aminobenzenesulfonic acid in the form of an inner salt was not confirmed. A scheme of the conjugation of the molecule of p-aminobenzenesulfonic acid is proposed.

LITERATURE CITED

[1] O.Yu. Magidson, Progr. Chem. 15, 101 (1946).

[2] E.H. Northey, Sulfonamides (1948) 5.

[3] V. Meyer, P. Jacobson, Lehrbuch d. Organischen Chemie (1902) II, 1, 211.

[4] B.N. Menshutkin, Carbocyclic Compounds (Moscow-Leningrad, 1926), 78.

[5] A. E. Chichibabin, Fundamental Principles of Organic Chemistry (1932), 249.

[6] Richter-Anschütz, Chemie der Kohlenstoffvervindungen (1935) II, 199.

[7] A. Holleman, Course of Organic Chemistry (Moscow-Leningrad 1938), 385.

[8] P. Karrer, Organic Chemistry (Moscow, 1938), 502.

[9] N. Bjerrum, Z. physik.Chem. 104, 147 (1923).

[10] N.V. Sidgwicks, The Organic Chemistry of Nitrogen (1937), 72.

[11] L. Fieser and M. Fieser, Organic Chemistry (Moscow, 1949) 530.

[12] U. Pestemer and H. Flaschka, Monatsh. 71, 325 (1938).

[13] H. Böhme, J. Wagner, Arch. Pharm. 280, 255 (1942).

[14] Grammaticakis, Bull. soc. chim. 1954, 92.

[15] N.A. Valyashko and F.F. Cheshko, J. Gen. Chem., Supp. Vol. I, 584 (1953).

[16] N.A. Valyashko, J. Russ. Chem. Soc. 42, 751,961 (1910).

[17] N.A. Valyashko and Yu. S. Rozum, J. Gen. Chem. 17, 756 (1947).

[18] N.S. Kurnakov, Introduction to Physicochemical Analysis (1940), 191.

[19] W.D. Kumler and L.A. Streit, J. am. Chem. Soc. 65, 2349 (1943).

[20] T. Wohlfahrt, J. prakt. Chem. 66, 551 (1902).

[21] L. Demeny, Rec. trav. chim. 48, 1146 (1929).

[22] R. Kuhn and H. Ruelius, Ber. 83, 420 (1950).

[23] G. Devoto, Atti Linc. 19, 50 (1934).

[24] I. A. Kablukov, Thermochemistry (1931), 128.

[25] G. Massol, Compt. rend. 132, 1572 (1901).

[26] W. Swientoslawski, Ber. 43, 1498 (1916).

[27] A. Springer and H.C. Jones, J. Am. Chem. Soc. 48, 438 (1912).

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ABSORPTION SPECTRA AND STRUCTURE OF BENZENE DERIVATIVES

XXI. p-DIMETHYLAMINOBENZENESULFONIC ACID AND ITS METHYL ESTER

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Following on our discovery [1] that p-aminobenzenesulfonic acid does not exist in the form of an inner salt or dipolar ion, it was necessary to investigate the "sulfanil-betaines" described in the literature [2-5]; these are the betaine forms of the methyl ester of p-dimethylaminobenzenesulfonic acid. Investigation of the free acid was also desirable.

p-Dimethylaminobenzenesulfonic acid was prepared for spectrographic investigation by methylation of p-aminobenzenesulfonic acid with methyl iodide by the Griess method [2]. The methyl ester of p-dimethylaminobenzenesulfonic acid was synthesized by the method described [6], but modified slightly in that we immediately treated the reaction mixture of p-aminobenzenesulfonic with water after heating with dimethyl sulfate and extracted the methyl ester of p-dimethylaminobenzenesulfonic acid with ether.

Spectrographic investigation of p-dimethylaminobenzenesulfonic acid. The absorption spectrum was examined in 40 % ethanol solution at a concentration of 10^{-2}-10^{-5} M (Fig. 1, curve 3). The results show that the character of the absorption spectrum of p-aminobenzenesulfonic acid is also retained when the hydrogen atoms of the amino group are substituted by methyl radicals. The absorption is shifted by 100-150 A in the long-wave direction, as in the case of the ethyl ester of p-aminobenzene sulfonic acid, in comparison with the absorption of p-aminobenzenesulfonic acid, and the intensity of the absorption maximum is also increased. The maximum is likewise shifted towards the long-wave region (by 60 A) (Table 1).

TABLE 1

Absorption band (in 40 % ethanol)	Maximum		Minimum		Inflection of curve	
	λ	ε	λ	ε	λ	ε
p-Aminobenzene-sulfonic acid	2500	16600	2380	6400	3120—2900	50—360
p-Dimethyl-aminobenzene-sulfonic acid	2560	24000	2390	7500	3085—2950	100—640

A similar displacement of the absorption spectrum toward the long-wave region occurs when methyl groups are introduced into the amino group of the aniline molecule, as shown by Baly and Collie [7] who investigated the absorption spectra of methyl and dimethyl derivatives of aniline. Robertson and Matsen [8] later compared the spectra of aniline and its methyl derivatives (amino-substituted) and established that substitution of the H atoms of the amino group intensifies and displaces the absorption towards the long-wave region.

The absorption spectrum of p-dimethylaminobenzenesulfonic acid was also investigated in 1 N HCl solution at concentrations of 10^{-2} - 10^{-3} M (Fig. 1, curve 5). Formation of a salt of p-dimethylaminobenzenesulfonic

* Deceased.

acid with hydrochloric acid sharply changes the spectrum which now approaches the φ band of the spectrum of benzenesulfonic acid since the conjugation of the dimethylamino group with the benzene ring and with the sulfonic group is destroyed and there remains only the conjugation of the benzene ring with the sulfonic group:

$$(CH_3)_2\ddot{N}-C_6H_4-SO_3H + H^+ + Cl^- \longrightarrow \left[(CH_3)_2\overset{+}{\underset{\uparrow}{N}}\overset{H}{}-C_6H_4-SO_3H\right] Cl^-.$$

Formation of a salt with hydrochloric acid is spectrographically reflected in a fall in the intensity of the absorption band of p-dimethylaminobenzenesulfonic acid by a factor of 48.

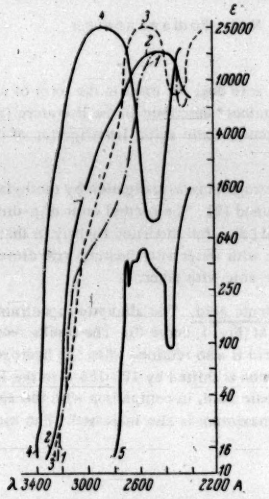


Fig. 1. Absorption spectra of p-aminobenzenesulfonic acid, p-dimethylaminobenzenesulfonic acid, and their esters.

1) p-Aminobenzenesulfonic acid in 40% ethanol (10^{-2} – 10^{-4} M), 2) ethyl ester of p-aminobenzenesulfonic acid in 95% ethanol (10^{-2} – 10^{-4} M), 3) p-dimethylaminobenzenesulfonic acid in 40% ethanol (10^{-2} – 10^{-5} M), 4) methyl ester of p-dimethylaminobenzenesulfonic acid in 40% ethanol (10^{-2} – 10^{-5} M), 5) p-dimethylaminobenzenesulfonic acid in 1 N HCl (10^{-2} – 10^{-3} M).

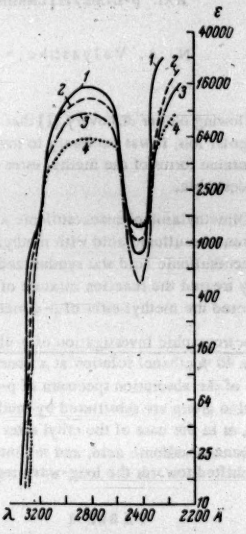


Fig 2. Absorption spectra of the methyl ester of p-dimethylaminobenzenesulfonic acid in 40% ethanol after standing.

1) Freshly prepared (10^{-2} – 10^{-5} M), 2) after 8 days' standing (10^{-2} – 10^{-5} M), 3) after 17 days' standing (10^{-2} – 10^{-5} M), 4) final form isolated after change of the crystals (10^{-2} – 10^{-5} M).

EXPERIMENTAL

Investigation of the methyl ester of p-dimethylaminobenzenesulfonic acid. The methyl ester, freshly prepared and recrystallized from 40% ethanol, is in the form of fine, white, acicular crystals with m.p. 91°; soluble in ethanol, ethyl ether and benzene, insoluble in water. The crystals alter in melting point and solubility on standing. Attention was first directed to this characteristic by Kuhn and co-workers [4,5] who believed that on

standing, the crystals of the methyl ester of p-dimethylaminobenzenesulfonic acid are transformed into an isomeric compound with a dipolar ion – the betaine of p-dimethylaminobenzenesulfonic acid.

We have therefore undertaken a more detailed investigation of the methyl ester of p-dimethylaminobenzenesulfonic acid and of its transformations. The absorption spectra of the ester in the freshly prepared state and after 8 and 17 days' standing were examined. A study was also made of the new form (soluble in water and insoluble in benzene, and not containing any trace of the original ester) which was extracted with benzene after completion of the transformation.

Results of the investigations are set forth in Table 2.

When the preparation melting at above 250° is recrystallized from 40% aqueous ethanol, the substance with m.p. 91° is again formed, i.e. the methyl ester of p-dimethylaminobenzenesulfonic acid.

TABLE 2

Substance	Melting point	Intensity of absorption ϵ at 2850 A
Methyl ester of p-dimethyl-aminobenzenesulfonic acid		
after 24 hours	91°	24000
after 3 days	180	—
after 8 days	230 (decomp.)	20000
after 17 days	250 (decomp.)	14800
New form, soluble in water, purified by extraction with benzene	300 (decomp.)	8300

The absorption spectra of the methyl ester of p-dimethylaminobenzenesulfonic acid were investigated in 40% ethanol at concentrations of 10^{-2} to 10^{-5} M. The curves of the absorption spectra of the methyl ester of p-dimethylaminobenzenesulfonic acid after the crystals stood for 8 and 17 days, and the curves of the pure form obtained by modification of the crystals of the methyl ester of p-dimethylaminobenzenesulfonic acidon standing, retain the character of the absorption of the original ester (Fig. 2, curves 1-4). The maxima of the absorption bands lie at one and the same wavelength of λ 2850 A, and only the absorption intensity diminishes (by factors of 1.2 and 1.6) as seen in Table 2.

The progressive changes in the crystals of freshly prepared methyl ester of p-dimethylaminobenzenesulfonic acid in the solid state were also investigated under the microscope. A drop of solution of freshly prepared ester in 40% ethanol was transferred to an object glass, subjected to unforced evaporation and examined at definite intervals of time (after 8 and 17 days' standing) (Fig. 3, photomicrographs 1-3). The methyl ester of p-dimethylaminobenzenesulfonic acid was also examined after 17 days' standing of a preparation washed with benzene for removal of the original form of the ester (photomicrograph 4). The photomicrographs were taken in a GOI polarization microscope with the help of a Leitz film pack and FED film, with which preliminary threefold magnification was effected. A no. 40 objective with a 6.5 X lens was used. The photomicrographs provide a picture of the progressive change of the crystal form of the substance.

The freshly prepared, benzene-soluble form (photomicrograph 1) consisted of well defined long prisms up to 0.4-0.5 mm in length and about 0.015 mm across. The crystals were uniaxial and postitive with weak double refraction. The form of the original crystals changed in course of standing (8 days) when the solubility in benzene fell by a factor of 2 (48.2%) and crystals soluble in water (49.3%) were developed. The edges of the prisms undergo modification (photomicrograph 2) and fine isometric plates appear which are likewise uniaxial and positive, but with a higher index of refraction. The plates formed belong to the second modification of the methyl ester of p-dimethylaminobenzenesulfonic acid. After 17 days, when the solubility of the crystals in benzene has fallen

to 21% and that in water has risen to 78.8%, the crystal form changes even more markedly (photomicrograph 3). The original prisms change into well marked dendritic forms. In its final form, after 17 days' standing (and washing with benzene for elimination of the original form) the methyl ester of p-dimethylaminobenzenesulfonic acid (photomicrograph 4) consists of fine isometric-lamellar crystals.

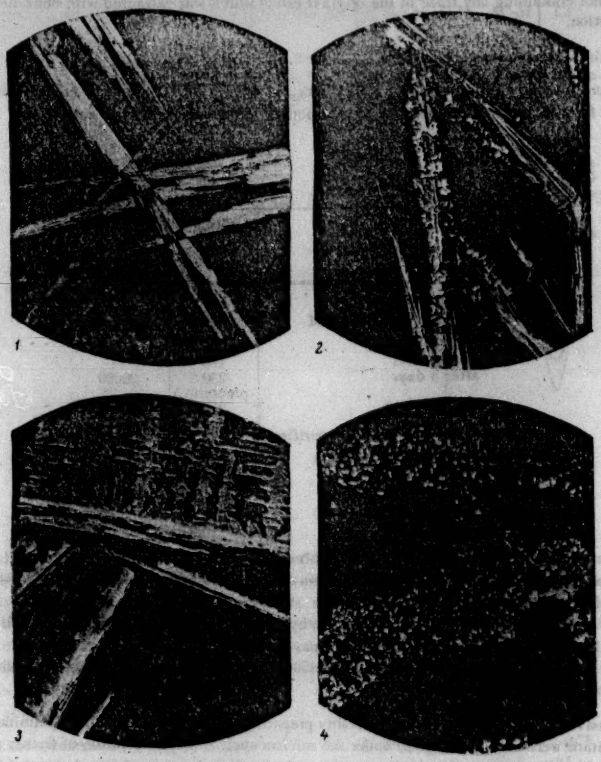


Fig. 3. Photomicrographs of the methyl ester of p-dimethylaminobenzenesulfonic acid.

1) Freshly prepared methyl ester 800 x (crossed nicols); 2) methyl ester after 8 days' standing, breakdown of the edges of the prismatic crystals is observed, 800 x (crossed nicols); 3) methyl ester after standing for 17 days, prismatic crystals change into well defined dendritic forms, 800 x (crossed nicols); 4) methyl ester after 17 days' standing, washed with benzene for removal of unchanged original form, 800 x (crossed nicols).

The following materials were examined by the x-ray method: the freshly prepared methyl ester of p-dimethylaminobenzenesulfonic acid, soluble in benzene; the product kept for 17 days in benzene, not soluble and containing 78.8% of the modified form; the product kept for 17 days and washed with benzene for elimination of the

unmodified original form of the ester. 'Crystalline powders were obtained by precipitation from solutions saturated at 20°. Debye-grams were plotted with the help of monochromatic x-rays (λ 1.934 A) with an iron anticathode in a short-focus Pines x-ray tube.

The x-ray diffraction spectrum (debye-gram) of the freshly prepared pulverulent benzene-soluble form contains several diffraction maxima. Debye-gram 1 (Fig. 4) represents the diffraction spectrum of the original crystalline form of the methyl ester of p-dimethylaminobenzenesulfonic acid. Increasing storage period (17 days) and decreasing solubility of the crystals in benzene are accompanied by development of solubility in water and change in the character of the debye gram. The diffraction maxima are narrowed, and their position changes (debye-gram 2). The gradual and steady change of the diffraction spectrum testifies to gradual accumulation of the second crystalline form of the methyl ester of p-dimethylaminobenzenesulfonic acid. Debye-gram 2 thus represents the spectrum of a mixture of both crystalline forms. After 17 days, when the solubility of the crystal mixture in water rises to 78.8%, after washing with benzene for elimination of residues of the benzene-soluble form, the change in the x-ray diffraction reaches a certain limit. The diffraction maxima become sharper. Debye-gram 3 represents the diffraction spectrum of the second crystalline form of the methyl ester of p-dimethylaminobenzenesulfonic acid. The different interference patterns of the two modifications are in harmony with the visual difference in intensity of the maxima of the diffraction bands of both spectra.

The characteristic data for the interatomic distances of both modifications of the methyl ester of p-dimethylaminobenzenesulfonic acid, as measured by the x-ray method, are given below:

1st modification d = 4.4, 3.5, 3.25, 2.6 A;
2nd modification d = 3.05, 2.4, 1.96 A.

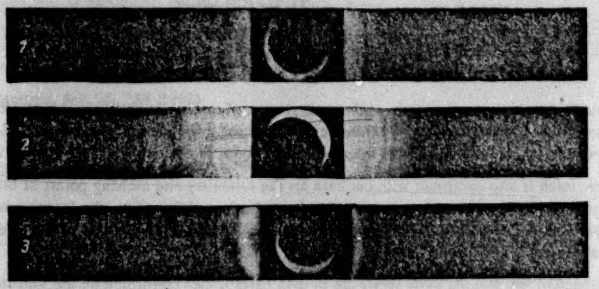


Fig. 4. Debye-grams of crystals of the methyl ester of p-dimethylaminobenzenesulfonic acid.

1) freshly prepared methyl ester of p-dimethylaminobenzenesulfonic acid; 2) methyl ester of p-dimethylaminobenzenesulfonic acid after 17 days' standing; 3) methyl ester after 17 days' standing, washed with benzene for removal of unchanged original form.

Evaluation of Results of Investigation of the Methyl Ester of p-Dimethylaminobenzenesulfonic Acid.

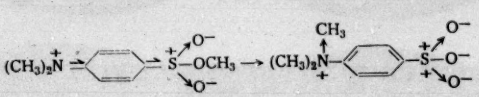
Willstätter [9] indicated the possibility of isomerism in the series of methyl esters of sulfonic acids of the aliphatic series and of the existence of betaines. Kuhn and Brydowna [4] studied the action of diazomethane on aminoacids in order to check Bjerrum's theory [10] of the dipolarity of aminosulfonic acids. Reaction of diazomethane with p-aminobenzenesulfonic acid gives, apart from the methyl ester of the acid, a compound differing in physical properties from the ester that Kuhn and Brydowna assumed to be the betaine of p-aminobenzenesulfonic acid. Kuhn and Ruelius [5] point out that this last compound is identical with the product obtained [6]

by the action of dimethyl sulfate on p-aminobenzenesulfonic acid. According to Devoto [3], methyl iodide may act on p-aminobenzenesulfonic acid in presence of sodium carbonate to give the betaine of p-aminobenzenesulfonic acid. On repeating this synthesis we failed to confirm Devoto's claim. The reaction gave p-dimethylaminobenzenesulfonic acid which was investigated spectrographically.

It must be noted that the above cited investigators did not isolate the hypothetical betaine and did not determine its structure. The hypothesis of the formation of a betaine originated from their attempts to account for the experimental results – the change of solubility and melting point of the ester.

Our spectrographic investigations of the methyl ester of p-dimethylaminobenzenesulfonic acid (Fig. 2, Curves 1-4) do not confirm its transformation into a betaine as was suggested by Kuhn and Ruelius. Spectrographic investigations of solutions of medium concentration permit the possibility of judging the state of the molecule. Fig. 2 (Curves 1-3) shows that after 17 days in storage the absorption of the methyl ester of p-dimethylaminobenzenesulfonic acid did not change in character but only in intensity by a factor of 1.5. The absence after this period of any sort of displacement of the absorption band toward the long waves testifies to the molecules of the methyl ester of p-dimethylaminobenzenesulfonic acid remaining intact.

Formation of a betaine, however, should have been accompanied by an abrupt change in the absorption spectrum and its approach to the spectrum of benzenesulfonic acid since the betaine should contain not the $\overset{+}{N}(CH_3)_2$ group but the $\overset{+}{N}(CH_3)_3$ group; in the latter case the unshared electron pair of the nitrogen atom would be bound and the conjugation with the benzene ring suppressed:



As shown by the absorption spectrum of the methyl ester of p-dimethylaminobenzenesulfonic acid after undergoing change, no transformation to a betaine occurs, but since the change in properties of the methyl ester occurs spontaneously in the solid crystalline state, we may suggest that a change in the crystal lattice is involved.

This conclusion is also consistent with our data for the solubility and melting points of the crystals after different periods of storage. Taking into account the sharp rise in melting point, the increase in solubility in water and the fall in solubility in benzene, we must conclude that the crystal lattice of the ester gradually changes from a molecular to an ionic lattice.

The presence of one and the same substance in both cases is also confirmed by the facility of reciprocal transition of the crystals with an ionic lattice into the crystals with a molecular lattice. Recrystallization of the ionic crystals from 40% ethanol again gives the original form of the ester with m.p. 91°; if it is fused and allowed to solidify, then the substance with the ionic lattice is obtained again with a decomposition point of about 300°.

The x-ray data are likewise consistent with the physical properties of both crystalline modifications of the methyl ester of p-dimethylaminobenzenesulfonic acid and with the results of microscopic examination. Two different x-ray diffraction spectra with gradual transition from one to the other indicate the existence of two different crystalline modifications which are enantiomorphs. The character of the x-ray diffraction spectra progressively changes when the powder form of the methyl ester is allowed to stand: the diffraction bands become narrower, their maxima become sharper, and their linear parameters alter. The character of the change of the x-ray diffraction spectrum is in harmony with the hypothesis of transition of the crystalline lattice of the freshly prepared ester from the molecular to the ionic type.

According to P. Niggli [11], molecular polymorphism occurs when there is a possibility of separating the different structures from one another, and when there is a marked discontinuous transition from one to the other. Both requirements are satisfied in the case of the methyl ester of p-dimethylaminobenzenesulfonic acid: both forms were separated and their reciprocal transition was observed.

What had been assumed without proof to be the betaine form is evidently the ionic form of the dimorphic methyl ester of p-dimethylaminobenzenesulfonic acid.

SUMMARY

1. The absorption spectra of p- dimethylaminobenzenesulfonic acid and its methyl ester were investigated; the spectra are similar to the spectra of p-aminobenzenesulfonic acid. It was established that the methyl ester of p-dimethylaminobenzenesulfonic acid does not exist in the betaine form.

2. A microscopic examination was made of the spontaneous transformation of crystals of the methyl ester into a high-melting water-soluble form – the stable form of the crystals.

3. An x-ray examination was made of crystalline powders of the methyl ester of the acid after standing for various periods of time.

4. The dimorphism of the methyl ester of p-dimethylaminobenzenesulfonic acid was established. It exists in two crystalline forms, one of which (stable) is characterized by an ionic lattice, and the other (unstable) by a moleuclar lattice. The transition of one form to the other was studied.

LITERATURE CITED

[1] N. A. Valyashko and N. P. Romazanovich, J. Gen Chem., 26, 2509 (1956) (T.p. 2801).*

[2] P. Griess, Ber. 12, 2116 (1879).

[3] G. Devoto, Chem. Zentr. 1934, I, 11.

[4] R. Kuhn and W. Brydowna, Ber. 70, 1333 (1937).

[5] R. Kuhn and H. Ruelius, Ber. 83, 420 (1950).

[6] J. Houben and G. Schreiber, Ber. 53, 2346 (1920).

[7] E. C. C. Baly and J. Collie, J. Chem. Soc. 87, 1332 (1905).

[8] B. Robertson and F. A. Matsen, J. Am. Chem. Soc. 72, 1543 (1950).

[9] R. Willstätter, Ber. 35, 584 (1902)

[10] N. Bjerrum, Z. Physik Chem. 104, 147 (1923).

[11] P. Niggli, Stereochemistry (Moscow, 1949), 215

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SYNTHESIS OF SOME HALOGEN-CONTAINING AMINO- AND NITRO DERIVATIVES OF BIPHENYL

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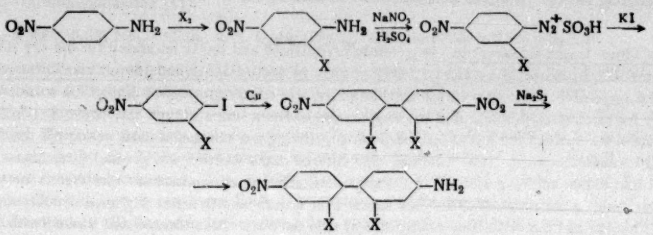
In the course of a kinetic investigation we had need of 4-amino-2,2'-dichlorobiphenyl, the analogous bromine-containing compound and their 4'-nitro derivatives. None of these substances has been described in the literature. We had in mind the following scheme for the preparation of the aminonitro compounds (X = halogen):



In this scheme the greatest interest from the preparative standpoint is attached to two stages – the formation of biaryl systems on treatment of the corresponding iodo derivatives with copper powder and the partial reduction of the 4,4'-dinitro-2,2'-dihalo derivatives of biphenyl. In the first case the condensation may be complicated by the presence in the benzene derivatives of atoms of other halogens (apart from iodine) which usually in the present reaction (the Ullmann reaction) can also react with copper under certain conditions even though they are less reactive than the iodine atom [1-4]. In the second case we must remember that, due to the weakening of the reactivity of substituents in the 4,4'-position in such derivatives of biphenyl in comparison with analogous compounds of the benzene series, certain difficulties could arise during the partial reduction of the dintro derivatives. However, after careful selection of the experimental conditions, we were able to obtain both the dinitro derivatives in question and their products of partial reduction.

We were struck by the extremely interesting properties of 4-amino-4'-nitro-2,2'-dihalobiphenyls. Whereas their hydrochlorides crystallize easily, the free bases themselves manifest a striking tendency to remain in the glassy state. We could not find any method of obtaining these substances in the crystalline form, although an especially thorough purification and the results of analysis conclusively demonstrate that we are dealing with products of a high degree of purity. It has recently been shown [7,8] that the glassy state may be inherent in pure organic compounds if they possess a high molecular weight and their molecules have a well marked asymmetric structure. Both our substances satisfy these requirements.

The synthesis of 4-nitro-2,2'-dihalo derivatives needed for the preparation of the corresponding amines was effected by deamination of 4-amino-4'-nitro-2,2'-dihalobiphenyls. Two methods were tried (in the case of

the bromo derivative) – reduction of the diazo compound with alcohol in presence of cuprous oxide and reduction with hypophosphorous acid; losses bound up with purification operations were lowered by not isolating the 4-nitro-2,2'-dihalobiphenyls in the pure state but by subjecting them to the reduction stage in the crude form. In both cases the expected 4-amino-2,2'-dihalo derivatives of biphenyl were obtained. Due to the simplicity of the operations, we consider deamination with the help of hypophosphorous acid to be preferable.

EXPERIMENTAL

I. Synthesis of 4-Amino-4'-nitro-2,2'-dichlorobiphenyl and 4-Amino-2,2'-dichlorobiphenyl

a) 2-Chloro-4-nitroaniline. Our experiments did not confirm the literature claim [9] that this substance is formed on chlorination of p-nitroaniline in boiling hydrochloric acid. Under the conditions described we always obtained predominantly 2,6-dichloro-4-nitroaniline. We were only able to obtain satisfactory results by maintaining the following conditions.

To 40 g p-nitroaniline was added 1200 ml water and 200 ml concentrated hydrochloric acid; the mixture was heated until the amine had completely dissolved and was then rapidly cooled to room temperature. Through the resultant suspension was passed a gentle stream of chlorine (with vigorous mechanical stirring) until an equimolar amount had combined (increase in weight of 20-21 g). The precipitate was separated from the liquid, and the 2-chloro-4-nitroaniline was extracted from it with several portions of boiling dilute hydrochloric acid (1 : 2) in which the 2,6-dichloro-4-nitroaniline formed as a by-product is substantially insoluble. The precipitate formed on cooling was recrystallized from hot water containing a little ammonia. Yield of amine 25 g (50%). M. p. 104°.

b) 2-Chloro-4-nitroiodobenzene. 48 g freshly crystallized and finely triturated (in the dry state) 2-chloro-4-nitroaniline was suspended in a cooled (8-10°) mixture of 480 ml water and 160 ml concentrated sulfuric acid. To the suspension, vigorously stirred mechanically, was slowly introduced dropwise a solution of 20g sodium nitrite in 80 ml water at such a rate that the temperature of the mixture did not rise above 8-10° (external cooling). After the whole of the nitrite had been added, stirring was continued until nearly all the solid particles dissolved; this required usually 20-30 minutes. The filtered diazo solution was gradually run into a solution of 100 g potassium iodide and 50 g iodine* in 100 ml water, after which the mixture was heated for an hour on a boiling water bath. After removal of the free iodine with solium bisulfite (heating until decolorized), the mixture was cooled and the crystalline precipitate of iodo derivative was filtered and washed with water. Yield 66 g (84%). After recrystallization from methanol the substance had m.p. 99-100° (the literature [11] gives 103°).

c) 4,4'-Dinitro-2,2'-dichlorobiphenyl. Only one reference to this compound appears in the literature [12], and this omits all details of the synthesis. 25 g electrolytic copper powder** activated with a solution of iodine in acetone [16] was added to 25 g fused 2-chloro-4-nitroiodobenzene heated to 210° in a large test tube of heat-resistant glass immersed in a metal bath. This addition was effected slowly over aperiod of 30-40 minutes. The powder was added at such a rate that the temperature of the melt did not rise above 220° (thermometer in melt), and the mixture was held at this temperature for another 2 hours. Periodic stirring of the melt with a copper rod is necessary during the process of addition of the copper. The product of reaction was extracted with several portions of boiling toluene (in all 300-400 ml), after which the solvent was distilled off, and the contents of the flask treated with steam to remove residues of toluene and unreacted starting substance. The remainder was distilled with superheated steam. The main bulk of reaction product comes over in the distillate in the form of a light yellow oil at 160-200° and soon crystallizes on cooling. M. p. 107° after recrystallization

* The advantage of using iodine in such cases is discussed in the paper [10].

** It is known that the success of the reaction of formation of biaryl systems by treatment of the appropriate halogen derivatives with copper powder depends to a considerable extent upon the method of preparation of this powder [2]. The grade of copper powder known as "natural copper C" has been particularly recommended [1]. We did not have this grade at our disposal, but after some tests in known reactions we found that electrolytically precipitated copper powder (both commercial and laboratory preparations [13]) is not inferior in quality to the above mentioned grade. The reaction goes extremely slowly with copper powder prepared in the usual manner by the action of zinc dust on copper sulfate solution [14]. Somewhat better results than in the latter case, but still rather unsatisfactory, were obtained with copper prepared by reduction of copper sulfate with the help of chromium chloride [15].

from methanol (the literature [12] reports 107-108°). Yield about 6 g (43.5 %).

d) 4-Amino-4'-nitro-2,2'-dichlorobiphenyl. To a solution of 6 g 4,4'-dinitro-2,2'-dichlorobiphenyl in 600 ml methanol, heated to 40° (thermometer in liquid) was added dropwise, with shaking, 30 ml 1 M solution of sodium disulfide in aqueous methanol • at such a speed that the temperature was held at 40-41°. After addition of the whole of the disulfide, the mixture was held for another 10 minutes at the same temperature and acidified with concentrated hydrochloric acid; the whole of the solvent was then evaporated. The amine was extracted with small portions of boiling dilute hydrochloric acid (1 : 1). 4.2 g (69 %) of the amine hydrochloride came down from the cooled solution. The product was recrystallized three times from hydrochloric acid (the first time with carbon) of the same concentration and dried in a vacuum desiccator. The hydrochloride melts at 204-206°. The free amine was obtained by heating 3 g of the dry product with concentrated ammonia. The amine was obtained in the form of a light yellow oil which was washed several times with distilled water and dried in a vacuum desiccator where it solidified to a glassy mass. The product was then dissolved in 25 ml methanol and the solution was filtered to remove any mechanical impurities. Precipitation was effected by addition of 75 ml distilled water. Reprecipitation was effected with 15 ml methanol + 45 ml water. The oily product was dried in vacuum at 65° (in methanol vapor); even after standing for 3 years it did not crystallize, and at low temperatures it formed a glassy mass.

4-Amino-4'-nitro-2,2'-dichlorobiphenyl is very highly soluble in all the common solvents; it dissolves with difficulty in water; its hydrochloride is fairly soluble in benzene from which it can be recrystallized. This ease of solubility is undoubtedly due to the asymmetry of the structure of the molecule. Boiling of the amine with a large excess of Na_2S_2 in methanol leads to its transformation in nearly quantitative yield into the known 2,2'-dichlorobenzidine [17].

Found %: N 9.87, 9.93; NH_2 ••5.66, 5.71. $C_{12}H_8O_2N_2Cl_2$. Calculated %: N 9.90; NH_2 5.66.

e) 4-Amino-2,2'-dichlorobiphenyl. 1) Deamination of 4-amino-4'-nitro-2,2'-dichlorobiphenyl. 3 g of 4-amino-4'-nitro-2,2'-dichlorobiphenyl hydrochloride was dissolved by heating in a mixture of 6 ml concentrated hydrochloric acid and 15 ml glacial acetic acid. The solution was quickly cooled to 0° and to the finely crystalline slurry was gradually added a solution of sodium nitrite (0.75 g $NaNO_2$ in 7.5 ml H_2O) cooled to 0°. The diazo solution was filtered and slowly run into an ice-cooled mixture of 12 g $NaH_2PO_2 \cdot H_2O$ and 12 ml concentrated hydrochloric acid. The reaction mass was well stirred and allowed to stand for 24 hours at room temperature in a loosely stoppered flask. The reaction product was isolated in the form of a viscous oil. The liquid was made alkaline with 10% caustic alkali and then poured off, while the oil was washed with water. The reaction product was extracted from it with several portions of boiling methanol until the last portion did not change color. In the residue was found a small amount of solid substance, insoluble in methanol; this was not further investigated. The combined methanol extracts were treated with carbon and the alcohol was completely distilled off. The residual yellow oil was dried in a vacuum desiccator where it formed a thick, consistent syrup. Yield 1.7 g. The syrup was subjected to the further operation of reduction.

2) Reduction of the product of deamination. 1.7 g of the product of deamination, obtained by the above-described method and placed in a small flask fitted with a reflux condenser, was dissolved in 17 ml warm ethyl alcohol; into this was run 1 ml of 100% hydrazine hydrate, and a very small pinch of Raney nickel [19] was added. A violent reaction commenced with foaming and the evolution of nitrogen. After the reaction had slowed down, ••• another 1 ml of hydrazine hydrate and a little more catalyst were added to the mixture. As the reaction died down, several further additions of catalyst were made until gas ceased to come off on intensive boiling.•••• The still warm solution was filtered and then treated with active carbon; the solvent was completely distilled off and the residue dried in a vacuum desiccator. The amine was extracted from the

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• Prepared in the following manner: 240 g $Na_2S \cdot 9H_2O$ and 32 g sulfur were gently heated with 500 ml water and 250 ml methanol until completely dissolved, and the cooled solution was diluted with water to 1 liter.

•• The micro method for determination of the aromatic amino group is described in the paper [18].

••• The course of the reaction can be conveniently regulated by following the intensity of evolution of gas bubbles through a glass capillary connected at one end with the help of a rubber tube to the upper part of the condenser; the other end of the glass capillary dips into a test tube containing about 0.5 ml water.

•••• The method of reduction of aromatic nitro compounds with hydrazine hydrate in presence of Raney nickel was proposed in 1953 by Balcom and Furst [20].

resinous residue with ligroine. The extract was treated with active carbon and 4-amino-2,2'-dichlorobiphenyl hydrochloride was isolated by passing dry hydrogen chloride into the solution. Yield of hydrochloride 1 g (39% calculated on 4-amino-4'nitro-2,2'-dichlorobiphenyl).

The hydrochloride of the amine was decomposed by heating with aqueous ammonia. The amine came down at first in the form of an oil but crystallized on cooling. M. p. 70-72°. The amine was further purified by dissolving it in ether and precipitating it as a salt by passage of a stream of dry hydrogen chloride. The hydrochloride was decomposed with ammonia and the amine washed by melting it under a layer of hot distilled water; the substance was then dissolved in boiling methanol (6 ml alcohol to 1 g amine) to which hot water was then gradually added until cloudy. The crystalline amine came down on cooling. This recrystallization was repeated several times until the melting point was constant at 73-74°.

Found %: NH_2 6.58, 6.62. $C_{12}H_9NCl_2$. Calculated %: NH_2 6.73.

4-Amino-2,2'-dichlorobiphenyl is a white crystalline substance, very easily soluble in common organic solvents, almost insoluble in water. The hydrochloride dissolves fairly readily in benzene.

II. Synthesis of 4-Amino-4'-nitro-2,2'-dibromibiphenyl and 4-Amino-2,2'dibromophenyl

a) 2-Bromo-4-nitroaniline. The compound was prepared by the known procedure [21]; the crude product was recrystallized from water.

b) 2-Bromo-4-nitroiodobenzene. 27 g 2-bromo-4-nitroaniline was dissolved by heating in a mixture of 230 ml conc. H_2SO_4 and 430 ml water. The solution was colled to +5° and was diazotized in the usual manner (13.5 g $NaNO_2$ in 44 ml water). The cooled and filtered diazo solution was slowly run into a solution of 22 g iodine and 44 g potassium iodide in 44 ml water. The subsequent operations were entirely analogous to those described for the preparation of 2-chloro-4-nitroiodobenzene. The yield was nearly quantitative. After recrystallization from methanol the compound had m.p. 107° (the literature [11] gives 106°).

c) 4,4'-Dinitro-2,2'-dibromobiphenyl. A large test tube containing 50 g 2-bromo-4-nitroiodobenzene was immersed in a metal bath heated to 200-210°. To the resultant melt was gradually added in the course of 75 minutes, with frequent sitrring of the content of the test tube with a copper rod, 50 g of electrolytic activated copper (see I, c) at such a rate that the temperature was held at 200-210° and never rose higher, as was especially to be feared at the instant of addition of the copper powder (thermometer in reaction mass). After the whole of the copper had been added, the mixture was held at the stated temperature for another 3 hours (periodic stirring). The reaction product was extracted with several portions of boiling toluene (in all 800-900 ml). The toluene and solution was twice treated with activated carbon and the solvent driven off to leave a very small volume. The residue was distilled with superheated steam, the following fractions being collected: 1st to 160°, 2nd 170-190°, 3rd 190-200°, and 4th 200-220°. The 1st fraction contained tolune and sometimes a little of the unreacted starting substance. The 2nd, 3rd and 4th fractions, consisting of a syrupy liquid, crystallized slowly in course of time, and mainly contained 4,4'-dinitro-2,2'-dibromobiphenyl in various degrees of purity. The 3rd fraction was dissolved in a large volume of methanol, the solution was twice treated with active carbon and the alcohol evaporated off to a small volume but not to the extent of causing separation of the oily substance from solution. After standing for some time (2-3 days), pure 4,4'-dinitro-2,2'-dibromobiphenyl crystallized from solution. A further quantity of product was obtained from the spent carbon and from the evaporated mother liquor.

The 2nd and 4th fractions were combined and redistilled in superheated steam. In this manner another 190-200° fraction was collected and the substance was purified as described above. Total yield 7 g (23%). Light yellow crystals with m.p. 126°.

Found %: N 7.00, 7.05. $C_{12}H_6O_4N_2Br_2$. Calculated %: N 6.97.

d) 4-Amino-4'-nitro-2,2'-dibromobiphenyl. 15.2 ml of 1 M aqueous methanolic solution of sodium disulfide (see I,e) was added dropwise with shaking to a solution of 3.8 g 4,4'-dinitro-2,2'-dibromobiphenyl in 380 ml gently boiling methanol. After all had been added, the solution was boiled for another 10 minutes. The mixture was acidified with concentrated hydrochloric acid, and the reaction product was separated and purified in exactly the same manner as for the analogous chlorine-containing compound. Yield of amine hydrochloride 2.7 g (70%); m.p. 220-222°.

4-Amino-4'nitro-2,2'-dibromobiphenyl likewise could not be obtained in the crystalline form; after

prolonged drying in vacuum at 65°, it consisted of a yellow, glassy mass whose properties were quite similar to those of 4-amino-4'-nitro-2,2'-dichlorobiphenyl; similarly to the latter, this amine can easily be transformed into the known 2,2'-dibromobenzidine [22].

Found %: NH_2 4.28, 4.27. $C_{12}H_8O_2N_2Br_2$. Calculated %: NH_2 4.31.

e) 4-Amino-2,2'-dibromobiphenyl. 1) Deamination of 4-amino-4'-nitro-2,2'-dibromobiphenyl with the aid of alcohol and cuprous oxide. 0.4. g of the hydrochloride of 4-amino-4'-nitro-2,2'-dibromobiphenyl was dissolved in 1.6 ml glacial acetic acid with addition of 3-5 drops of pyridine (for binding the hydrochloric acid – otherwise the substance does not dissolve) with heating on a water bath. The solution was cooled to 0° and slowly run into an equally cooled solution of sodium nitrite in concentrated sulfuric acid at such a rate that the temperature did not rise above 10-15°. The latter solution was prepared as follows: 0.09 g previously well dried and finely pulverized nitrite was gradually added with stirring to 0.6 ml cooled sulfuric acid (d 1.84); when the whole of the nitrite had been added, the mixture was cautiously heated at 60-70° until solution was complete, and then quickly cooled.

After addition of the amine solution to the nitrite, the mixture stood for 30 minutes (periodic shaking), after which the diazo solution was gradually run in the course of about 10-15 minutes at a temperature not exceeding 20° into a vigorously shaken suspension of 0.3 g cuprous oxide [23] in 2,5 ml anhydrous ethyl alcohol; nitrogen was evolved during this operation and the temperature rose spontaneously. The mixture was subsequently refluxed on a water bath for 1 hour and after filtration the alcohol was evaporated to a small volume.* The residue was made alkaline with 10% NaOH, and the reaction product taken up with ether. The ethereal extract was washed with water and treated with active carbon and dried over anhydrous Na_2SO_4. The ether was evaporated off completely and the residual oil dried in a vacuum disiccator after which it acquired the consistency of a viscous syrup. The reaction product was extracted from this with boiling methanol. After treatment of the alcohol solution with active carbon, the solvent was evaporated to dryness and the alcoholic residue was dried in vacuum at 65°. Yield 0.23 g. The deamination product was subjected to further reduction in this form.

2) Deamination of 4-amino-4'-nitro-2,2'-dibromobiphenyl with the help of hypophosphorous acid. This operation was similar in all respects to the procedure for deamination of the chloro analog (see I e): The diazo solution of 4-amino-4'-nitro-2,2'-dibromobiphenyl, prepared from 2 g of the amine hydrochloride, 4 ml concentrated hydrochloric acid, 10 ml glacial acetic acid and 0.4 g $NaNO_2$ in 4 ml water, was treated with a mixture of 8 g $NaH_2PO_2 \cdot H_2O$ and 8 ml concentrated hydrochloric acid. Yield of crude syrupy product of deamination 1.4 g. This product was subjected in this form to the next operation of reduction.

3) Reduction of the product of deamination. All the operations were exactly the same as in the reduction of the chloro analog (see I e): A solution of 1.4 g of the deamination product in 20 ml ethyl alcohol was twice treated with hydrazine hydrate in 0.9 ml portions in presence of Raney nickel. The yield of hydrochloride of 4-amino-2,2'-dibromobiphenyl was 1 g (56% calc'd on the hydrochloride of 4-amino-4'-nitro-2,2'-dibromobiphenyl). Melting point of the purified amine 94-95°. A mixed specimen of the substances obtained by the two methods (deamination either with alcohol or with hypophosphorous acid) did not give a depression of melting point.

The properties of 4-amino-2,2'-dibromobiphenyl are very similar to those of its chlorine-containing analog.

Found %: NH_2 4.85, 4.90. $C_{12}H_9NBr_2$. Calculated %: NH_2 4.90.

* The method of deamination described was mainly based on the method proposed by Hodgson and Turner [24].

SUMMARY

1. The following compounds not previously described in the literature were synthesized: 4-amino-4'-nitro-2,2'-dichlorobiphenyl, 4-amino-2,2'-dichlorobiphenyl, 4,4'-dinitro-2,2'-dibromobiphenyl, 4-amino-4'-nitro-2,2'-dibromobiphenyl and 4-amino-2,2'-dibromobiphenyl Some of the properties of these compounds were studied; it was found, in particular, that 4-amino-4'-nitro-2,2'-dichlorobiphenyl and its bromo analog exist in a glassy state, which is most probably due to the marked asymmetry of their molecules.

2. New methods are proposed and known methods are improved for the preparation of a series of intermediate products needed for the synthesis of the compounds named above.

LITERATURE CITED

[1] F. Ullmann and J. Bielecki, Ber. 34, 2174 (1901).

[2] P. Fanta, Chem. Revs. 38, 139 (1946).

[3] W. Davey and R. Latter, J. Chem. Soc. 1948, 264.

[4] R. Carlin and E. Swakon, J. Am. Chem. Soc. 77, 966 (1955).

[5] L. M. Litvinenko and A. P. Grekov, Ukrain. Chem. J. 20, 194 (1954); Symposium: Problems of Chemical Kinetics, Catalysis and Reactivity (Acad. Sci. USSR Press, 1955), 860; Trans. Inst. Chem. Research, Kharkov State Univ. 14, 167 (1956).

[6] L. M. Litvinenko, S. V. Tsukerman, and A.P. Grekov, Proc. Acad. Sci. USSR 101, 265 (1955); Ukrain. Chem. J. 21, 510 (1955).

[7] A. V. Komandin, Sci. Records Moscow State Univ. 164, 123 (1953).

[8] S. R. Sergienko, Yu. A. Bedov, and L. V.Ratnikova, Proc. Acad. Sci. USSR 102, 101 (1955).

[9] B. Flürscheim, J. Chem. Soc. 93, 1773 (1908).

[10] A. Baeyer, Ber. 38, 2760 (1905).

[11] G. Körner and A. Contardi, C. A. 8, 74 (1914).

[12] F. Case and R. Schock, J. Am. Chem. Soc. 65, 2087 (1943).

[13] B. A. Borok, M. Yu. Balshin, and N. A. Gavrilov, Scientific Research Institute of Machine Building and Metalworking 1935, No. 3, 27.

[14] Yu. V. Karyakin, Pure Chemical Reagents (State Chem. Press, 1947), 330.

[15] J. Piccard and L. Larsen, J. Am. Chem. Soc. 34, 2007 (1917).

[16] Synthetic Organic Preparations 1952, 3, 217.

[17] J. Cain and P. May, J. Chem. Soc. 97, 723 (1910).

[18] L. M. Litvinenko and A.P. Grekov, J. Anal. Chem. 10, 164 (1955) (T.p. 153).*

[19] See [16], p. 338.

[20] D. Balcom and A. Furst, J. Am. Chem. Soc. 75, 4334 (1953).

* T. p. = C. B. Translation pagination.

[21] B. Nicolet and W. Ray, J. Am. Chem. Soc. 49, 1805 (1927).

[22] S. Gabriel, Ber. 9, 1407 (1876).

[23] See [14], p. 338.

[24] H. Hodgson and H. Turner, J. Chem. Soc. 1942, 748.

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PENTAPHENYLPHOSPHORUS

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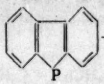
Organic compounds of elements of Group V with five radicals were recently obtained [1]. These radicals were covalently bound to the element. The valence-electron shell of such a compound is an unstable ten-electron system. Although the reactions of such compounds have great theoretical interest, their study has been neglected; we therefore resolved to undertake some systematic reactions with pentaphenylphosphorus (PPP), using both the literature data and the results of our own experiments.

Reactions of PPP can be arranged in three groups: 1) reactions with splitting-off of two phenyl groups and transition of P^{V} to P^{III}; 2) reactions with detachment of one phenyl group; 3) reactions with detachment of two phenyl groups without change of the valence of the phosphorus.

Reactions of the first group can go in two directions:

$$(C_6H_5)_5P \longrightarrow (C_6H_5)_3P + C_6H_5{-}C_6H_5,$$

$$(C_6H_5)_5P \longrightarrow \text{  } + 2C_6H_6.$$

Both reactions have previously been described [2] in connection with the thermal breakdown of PPP.

We carried out the decomposition of PPP in benzene solution. The first reaction then predominated. We noted, on carrying out the reaction in pyridine solution, that the second reaction predominated, P-phenyl-diphenylenephosphine being obtained in high yield.

Reactions of the second group are extremely numerous. They include reactions of PPP with HI and halogens [2]:

$$(C_6H_5)_5P + HI \longrightarrow (C_6H_5)_4PI + C_6H_6,$$
$$(C_6H_5)_5P + 2I_2 \longrightarrow [(C_6H_5)_4P]I_3 + C_6H_5I,$$

and the reactions with acetic acid that we investigated:

$$(C_6H_5)_5P + CH_3COOH \longrightarrow (C_6H_4)POCOCH_3 + C_6H_6,$$

as well as with halogenated solvents which take place even at the normal temperature and go fairly rapidly with heating or irradiation:

$$(C_6H_5)_5P + CHCl_3 \longrightarrow C_6H_6 + (C_6H_5)_4PCl + [CCl_2\cdot],$$
$$(C_6H_5)_5P + CCl_4 \longrightarrow C_6H_5Cl + (C_6H_5)_4PCl + C_2Cl_6,$$
$$(C_6H_5)_5P + C_2HCl_5 \longrightarrow C_6H_6 + (C_6H_5)_4PCl + C_2Cl_4.$$

The first reaction was described by Wittig [2], but the reaction products were described incorrectly.

To the third group belong the reactions of PPP with methanol and ethanol that we investigated:

$$(C_6H_5)_5P + 2ROH \longrightarrow 2C_6H_6 + (C_6H_5)_3P(OR)_2 \xrightarrow{H_2O} (C_6H_5)_3PO.$$

Scission of the phenyl group from phosphorus may go in two directions – either in the form of the phenyl anion or of the phenyl radical. Fixation on mercury is a very convenient means of demonstrating formation of the latter, and we made use of it in the present investigation. We did not observe the formation of diphenylmercury on decomposing PPP in benzene or pyridine while shaking with metallic mercury. We succeeded in isolating phenylmercurichloride when the reaction was carried out in CCl_4. Two reactions go simultaneously in this solvent: 1) reaction of the phenyl radical with CCl_4 with formation of chlorobenzene; 2) reaction of the phenyl radical with mercury. The latter predominates on energetic shaking with excess of mercury. On this basis the following scheme may be proposed for the reaction:

$$(C_6H_5)_5P \longrightarrow (C_6H_5)_4P\cdot + C_6H_5\cdot,$$
$$(C_6H_5)_4P\cdot + CCl_4 \longrightarrow (C_6H_5)_4PCl + CCl_3\cdot,$$
$$C_6H_5\cdot + CCl_4 \longrightarrow C_6H_5Cl + CCl_3\cdot,$$
$$C_6H_5\cdot + Hg \longrightarrow C_6H_5Hg\cdot,$$
$$C_6H_5Hg\cdot + CCl_4 \longrightarrow C_6H_5HgCl + CCl_3\cdot,$$
$$2CCl_3\cdot \longrightarrow C_2Cl_6.$$

In solvents containing hydrogen as well as halogen, e.g., $CHCl_3$ or C_2HCl_5, the reaction of PPP with mercury goes differently. The phenyl radical only reacts with the hydrogen of the solvent to form benzene, and fixation on mercury no longer takes place, the mercury undergoing chlorination. In chloroform, for example, calomel was detected. Chlorination may also serve as indication of the free-radical character of the process. As we know, chlorination of mercury is observed during breakdown of acyl peroxides in CCl_4 [3]. In our experiments the chlorination of mercury was especially intensive during the reaction of PPP in C_2HCl_5 and a considerable amount of the double salt $(C_6H_5)_4PCl \cdot HgCl_2$ could be isolated. The more complete chlorination is probably due to the action of atomic chlorine formed by breakdown of the C_2Cl_5 radical [4]:

$$C_6H_5\cdot + C_2HCl_5 \longrightarrow C_6H_6 + C_2Cl_5\cdot,$$
$$C_2Cl_5\cdot \longrightarrow C_2Cl_4 + Cl\cdot$$

Perchloroethylene was isolated from the products of reaction.

EXPERIMENTAL

PPP was obtained by Wittig's method [5] by the action of 1 N phenyllithium solution on an ethereal suspension of tetraphenylphosphonium iodide obtained by the method of Dodonoff [6]. After recrystallization from cyclohexane in a nitrogen atmosphere, PPP has decomp. p. 124°. PPP crystallizes with 0.5 mole cyclohexane.

Reaction with benzene. 7 g PPP and 30 ml benzene were heated in a nitrogen atmosphere at 80° for 1 hour. The solvent was driven off and the residue distilled with steam. In this manner 0.46 g (19.5%) diphenyl was isolated, m.p. 69.5° after recrystallization from methanol. A mixed specimen with pure diphenyl melted at 70°. The oily residue (4 g) was distilled with steam and then treated several times with HCl (1:1) for extraction of triphenylphosphine. Dilution of the hydrochloric acid filtrate with water caused 0.9 g (22.5%) triphenylphosphine to separate; m.p. 78° (from ethanol). The literature [7] gives m.p. 80°. A mixed melting test gave m.p. 78°. Sublimation in high vacuum of the HCl-insoluble residue at 100° gave P-phenyl-diphenylenephosphine (0.15g) which had m.p. 84° after recrystallization from methanol. The residue of 2.8 g was a glassy resin.

Reaction with pyridine. 6 g PPP in 40 ml pyridine was vigorously shaken in a nitrogen atmosphere for 150 hours. The solvent was distilled off, HCl being added to the first portions. This portion was later diluted with water. The benzene that separated was extracted with CCl_4; in solution in the latter it was converted by nitration to m-dinitrobenzene. The amount of the latter was 2 g (45.7% calculated on two diphenyl radicals), m.p. 88°. A mixed test gave no depression. The residue after distillation of the solvent

was steam-distilled to give 0.07 g diphenyl. From the oily residue (3.6 g) after steam distillation was isolated 2.2 g (60%) P-phenyl-diphenylene-phosphine with m.p. 83°; m.p. 91° after recrystallization from methanol. The literature [2] reports m.p. 93-94°. A mixed specimen with the P-phenyl-diphenylene-phospine obtained in the reaction with benzene did not give a depression. Found M (cryoscopic) 248.35. Calculated M 260.28. The infrared spectrum of P phenyl-phenylene-phosphine was found to be identical with that obtained previously [2]. The frequencies found in CS_2 solution were 13.27, 13.59, 13.73, 14.41. *

Reaction with acetic acid. 10 g PPP and 20 ml glacial acetic acid were heated 20 minutes. The benzene was distilled off with steam and extracted with CCl_4; it was then converted to m-dinitrobenzene, weight 2.2 g (60.4%); no depression of melting point in admixture with pure m-dinitrobenzene. The residue in the flask after the steam distillation was treated with KI to give 10 g of tetraphenylphosphonium iodide with m.p. 330°. The literature [6] reports m.p. 333°. No depression of melting point in admixture with a specimen prepared by Dodonoff's method.

Reaction with chloroform. 5 g PPP in 30 ml chloroform was left to stand in a nitrogen atmosphere for 2 days. After driving off the solvent, the residue was steam-distilled. Benzene came over with chloroform as well as with steam. It was nitrated to give 1.1 g m-dinitrobenzene (60.4% calculated on one phenyl radical), m.p. 87°. A mixed specimen with pure m-dinitrobenzene melted at 88°. A solution of potassium iodide was added to the aqueous solution containing tetraphenylphosphonium chloride (after the steam distillation) and the precipitate of tetraphenylphosphonium iodide was filtered off and dried. Yield 5.05 g (quantitative), m.p. 325°. After decolorization with animal charcoal and recrystallization from water, it had m.p. 330°. A mixed specimen with pure tetraphenylphosphonium chloride obtained by Dodonoff's method melted at 333°.

The reaction goes without heating and is accompanied by formation of an insignificant amount of resins. The same products are obtained when the reaction is effected by heating for 1 hour.

Photoreaction with chloroform. 5 g PPP and 30 ml chloroform were irradiated in a quartz test tube (20 mm diameter) with a PRK-2 ultraviolet lamp for 1 hour. The reaction products were separated by the same procedure as described above. 1.2 g (65.9%) m-dinitrobenzene was isolated with m.p. 87°, and tetraphenylphosphonium iodide was obtained in quantitative yield (5 g), m.p. 330°.

Thermal reaction with carbon tetrachloride. 5 g PPP and 35 ml carbon tetrachloride were heated in a flask in a nitrogen atmosphere for 1 hour at the boiling point of the solvent. The solvent wad distilled off. The residue was then steam-distilled; the first portions of distillate contained chlorobenzene together with carbon tetrachloride; the mixture was separated from the water and nitrated to give 1.4 g chlorodinitrobenzene (63.9%) with m.p. 42°. A mixture with β-4,1,3-chlorodinitrobenzene melted at 43°. Steam distillation gave 0.03 g diphenyl with m.p. 62°. A mixed specimen with pure diphenyl melted at 68°. As in the experiment with chlororform, tetraphenylphosphonium iodide was isolated in quantitative yield (5.1 g) with m.p. 330°. The same products were obtained when the reaction was preformed at the ordinary temperature and with shaking for 150 hours.

Photoreaction with carbon tetrachloride. 5 g PPP and 35ml carbon tetrachloride were irradiated in a quartz test tube (diameter 20 mm) with a PRK-2 ultraviolet lamp for 60 hours. The reaction products were separated by the same procedure as before. Yield 0.6 g chlorodinitrobenzene (27.3%) with m.p. 43.5°. A small amount of hexachloroethane was also obtained which had m.p. 183° after sublimation over conc. H_2SO_4; a mixed specimen with pure hexachloroethane melted at 185°. The yield of tetraphenylphosphonium iodide was quantitative.

Reaction with pentachloroethane. ** 11 g PPP and 50 ml pentachloroethane were charged into a flask with a ground-glass stopper in a nitrogen atmosphere. The reaction was completed in $1\frac{1}{2}$ - 2 hours at room temperature. The following fractions were isolated: 1st 80-100°; 2nd 100-130°, 3rd 130° and higher. From the 1st fraction was isolated benzene which was identified in the form of m-dinitrobenzene. Yield 2.5 g (62%) m-dinitrobenzene, m.p. 88°. A mixture with pure m-dinitrobenzene melted at 89°. Perchloroethylene was found in the second fraction. The constants were determined on fractions collected from several experiments, from which a fraction with b.p. 120-121° was separated after numerous fractionations. 41.3 g pentaphenylphosphorus gave 17.8 g perchloroethylene.

* The authors thank A. I. Finkelshtein for carrying out the infrared work.

**T.E. Vorontsova participated in this work.

d_4^{20} 1.6163, n_D^{20} 1.5035; literature data [8]: d_4^{20} 1.6226, n_D^{20} 1.5054.
Found %: Cl 84.76. M 169.09 Calculated %: Cl 85.52. M 165.85.

The 3rd fraction was pentachloroethane. The residue after distillation of the solvent – tetraphenylphosphonium chloride – was dissolved in water and converted into tetraphenylphosphonium iodide by treatment with KI. Yield 11.5 g (quantitative). M.p. 330° after recrystallization from water.

Thermal reaction with methyl alcohol. 5 g PPP was heated with 30 ml dry methyl alcohol in a sealed tube for 1 hour at 100°. The tube was opened, the solvent driven off and the residue distilled with steam. The first portions to come over, as well as the methanol that distilled off after the reaction, were diluted with water, and the separated benzene was extracted with carbon tetrachloride and nitrated. Yield 2.55 g m-dinitrobenzene (69.8% calculated on two phenyls), m.p. 89°. An insignificant amount of diphenyl with m.p. 62° came over during the steam distillation. A mixed sample with pure diphenyl melted at 68°. The triphenylphosphine oxide remaining behind after the steam distillation was extracted with methanol. Yield 3 g (quantitative) with m.p. 151° which rose to 153° after recrystallization from ethanol. According to the literature triphenylphosphine oxide melts at 153.5° [9]. A mixture with authentic triphenylphosphine oxide did not give a melting point depression. No resinification was observed during this reaction.

Thermal reaction with ethyl alcohol. 5 g PPP and 20 ml dry ethyl alcohol were placed in a tube which was then sealed and heated for 1 hour at 100°. The procedure for separation of the reaction products was similar to that described above. 2.33 g m-dinitrobenzene (63.8%) with m.p. 88° was obtained. The yield of triphenylphosphine oxide was 3 g (quantitative) with m.p. 148°, rising to 152° after recrystallization from ethanol. Traces of diphenyl were found, as in the preceding experiment. The same results were obtained when the reaction was performed at room temperature (5-6 days). Resinification was likewise not observed in these reactions.

Reaction of PPP with benzene in presence of mercury. 5 g PPP, 50 g mercury and 60 ml benzene in a nitrogen atmosphere were vigorously shaken for 150 hours. The benzene solution was separated from the finely dispersed mercury which was then washed several times with pure benzene. The subsequent procedure for separation of the reaction products was the same as in the reaction of PPP with benzene.

The products isolated were 0.3 g diphenyl (17.8%), 0.7 g triphenylphosphine (24.5%), and 0.1 g P-phenyl-diphenylene-phosphine. The residue consisted of resin (1.6 g). Diphenylmercury was not found in this reaction, nor was it found when PPP was reacted with pyridine in presence of mercury.

Reaction with mercury in carbon tetrachloride. a) 5 g PPP, 20 g mercury and 50 ml CCl_4 were placed in a shaking vessel in a nitrogen stream. The mixture CCl_4 was shaken at room temperature for 120 hours, after which the CCl_4 was separated. The mercury was washed twice with pure CCl_4 and the solvent was distilled off. The residue was steam-distilled. The first portions of distillate contained CCl_4 which was separated, and the C_6H_5Cl present in it was nitrated. Yield 0.2 g chlorodinitrobenzene with m.p. 43°. From the residue after steam distillation was also isolated a small quantity of phenylmercurichloride. The main portion of phenylmercurichloride (1.6 g = 46.9 %) was separated from the mercury by treatment with hot methanol. M. p. 243-248 °; no depression in admixture with the pure product. The residue after removal of the alcohol was diluted with water and reacted with KI to give 4.2 g (82.3%) $(C_6H_5)_4PI$, m.p. 325°, rising to 333° after recrystallization from water.

b) 5 g PPP, 80 g mercury and 50 ml CCl_4 were placed in a shaker and shaken at room temperature for 150 hours. The reaction products were separated as in the preceding experiment. They were C_6H_5HgCl 3.38 g (99.1%) and $(C_6H_5)_4PI$ 4.45 g (87.7%). A small quantity of calomel was also found.

Reaction with mercury in pentachloroethane. 5 g PPP, 40 ml pentachloroethane and 30 g metallic mercury were energetically shaken in a nitrogen atmosphere for 15 hours. The solvent was distilled off. The fraction up to 90° (containing benzene) was nitrated to give 0.5 g (27%) m-dinitrobenzene with m.p. 88°. A mixed specimen with pure m-dinitrobenzene did not give a depression. The last traces of pentachloroethane were removed by steam distillation. The aqueous layer in the distillation flask, containing tetraphenylphosphonium chloride, was treated with KI to give 1.6 g tetraphenylphosphonium iodide, m.p. 330°. Extraction with hot water of the solid residue in the flask gave 4.35 g (97%) of the double salt of mercuric chloride and tetraphenylphosphonium chloride, m.p. 212-213°; no depression in mixed test.

Found %: Cl 15.78, 15.68; Hg 32.23, 33.16. Calculated %: Cl 16.46; Hg 31.04.

SUMMARY

1. Reactions of pentaphenylphosphorus are classified on the basis of scission of the phenyl groups.

2. $(C_6H_5)_5P$ breaks down in benzene solution at the normal temperature and more rapidly on heating, $(C_6H_5)_5P$ with formation of $(C_6H_5)_3P$ and diphenyl; a small amount of P-phenyl-diphenylenephosphine is formed. The latter is the main product when the reaction is performed in pyridine solution.

3. $(C_6H_5)_5P$ in $CHCl_3$, CCl_4 and C_2HCl_5 solutions forms $(C_6H_5)_4PCl$; the C_6H_5 radical, binding the H of the solvent (in $CHCl_3$ and C_2HCl_5), gives benzene; in CCl_4 solution chlorobenzene is formed.

4. In alcholoic solution $(C_6H_5)_5P$ loses two phenyl radicals with formation of benzene. Triphenylphosphine oxide is quantitatively isolated after hydrolysis of the reaction products.

5. In presence of mercury, pentaphenylphosphorus in CCl_4 solution forms C_6H_5HgCl, and $(C_6H_5)_4PCl$, demonstrating the radical character of the process.

6. Chlorination of Hg is observed during breakdown of pentaphenylphosphorus in $CHCl_3$ or C_2HCl_5 in presence of mercury.

LITERATURE CITED

[1] G. Wittig and K. Torsell, Acta Chem. Scand. 7, 1293 (1953).

[2] G. Wittig and G. Geissler, Ann. 580, 44 (1953).

[3] O.A. Reutov and M.A. Besprozvanny, Proc. Acad. Sci. USSR 80, 765 (1951).

[4] G.A. Razuvaev and N.A. Osanova, J. Gen. Chem. 24, 1771 (1954) (T.p. 1741). *

[5] G. Wittig and M. Rieber, Ann. 562, 187 (1949).

[6] J. Dodonoff and H. Medox, Ber. 61, 907 (1928).

[7] Dictionary of Organic Compounds (1949), III, 887.

[8] Beilst. I, 187.

[9] A. Michaelis and V. Soden, Ann. 229, 295 (1885).

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STUDIES IN THE FIELD OF AZOMETHINE DYES

I. ON THE COLOR OF CERTAIN INDAMINE DYES DERIVED FROM α-NAPHTHOL, CONTAINING SUBSTITUENTS IN THE NAPHTHALENE NUCLEUS

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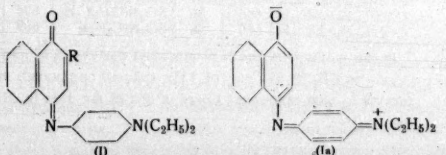
The relationship between the structure of indamine dyes derived from α-naphthol and their color has been comparatively little studied.

A. E. Porai-Koshits [1] and M. I. Krylova [2] have studied the absorption spectra of dyes derived from unsubstituted α-naphthol and 2-chloronaphth-1-ol. Later M. Pianka and H. S. Barany [3] measured the position of the absorption maxima of acetone solutions of the corresponding dyes from the esters of 1-hydroxy-2-naphthoic acid. Schultze [4] and recently Vittum and Weissberger [5] have studied the absorption spectra of indamine dyes from several derivatives of α-naphthol and substituted amides of 1-hydroxy-2-naphthoic acid in gelatine layers.

It seemed of interest to study in more detail the influence of the nature of substituents in the chromophore of such inner-salt dyes on their color. In this connection we synthesized a series of compounds of structure (I) and studied the absorption spectra of their alcoholic solutions [6] (see also [7]).



(I) (Ia)

R = H, Cl, Br, $COCH_3$, COOH, $COOCH_3$, $CONH_2$, $CONHC_2H_5$, $CONHC_6H_5$, $CONHC_{10}H_7$(α- and β-), $CON(C_2H_5)_2$, $CON(CH_3)C_6H_5$, $CON(C_6H_5)_2$, $CON(C_2H_5)C_{10}H_7$(α- and β-), $SO_2NHC_6H_5$, $SO_2N(C_2H_5)C_6H_5$, $SO_2N(C_2H_5)_2$.

The amides of 1-hydroxy-2-naphthoic acid necessary for the synthesis of the dyes were obtained by the following methods. The monosubstituted aryl amides were obtained by heating the corresponding amines with phenyl 1-hydroxy-2-naphthoate at low pressures (see [4]). The disubstituted amides and the ethyl amide were synthesized by the action of the amines on 1-hydroxy-2-naphthoyl chloride in inert solvents (see [8,9]). The substituted amides of 1-naphthol-2-sulfonic acid were obtained by the action of the corresponding amines on 1-naphthol-2-sulfonyl chloride, which proved to be easily formed by heating the salts of 1-naphthol-2-sulfonic acid with phosphorus pentachloride. By the action of 1-naphthol-2-sulfonyl chloride on ethylamine and diethylamine, instead of the expected sulfonamides there was obtained a high-melting material, which was apparently the product of the interaction of several molecules of naphtholsulfonyl chloride, involving the elimination of hydrogen chloride (see [10]).

The dyes were obtained by the oxidation with silver chloride of a mixture of diethyl-p-phenylenediamine and α-naphthol or its derivative in a solution of aqueous alkali and alcohol (see [11]). On oxidation in these

*Deceased.

conditions of a mixture of diethyl-p-phenylenediamine and α-naphthol, with subsequent crystallization of the product obtained from propanol, a dye was obtained (λ_{max} in C_2H_5OH 625 mμ) in which the nitrogen content corresponded to naphthol blue (I, R = H [6]). A more detailed study showed, however, that on oxidation of the above-mentioned substances with silver chloride there was formed, together with naphthol blue, a series of other blue dyes, and the preparation previously obtained by us was not fully purified from them. Naphthol blue (I, R = H) in a perfectly pure state (λ_{max} in C_2H_5OH 607 mμ can be obtained by chromatographic separation of the reaction product in benzene solution on aluminum oxide, in which this dye is desorbed first. Study of the other dyes obtained in this reaction is being continued. It is interesting to note that the color of one of them, whose adsorption on silica gel is close to naphthol blue (λ_{max} in CH_3OH 635 mμ), deepens, in contrast to the latter, on lowering the dielectric constant of the solvent (λ_{max} in C_6H_6 657 mμ) but is raised appreciably by the presence of alkali (λ_{max} in CH_3OH and NaOH 587 mμ).*

In the synthesis of dyes from 2-acetylnaphthol, 2,4-dibromonaphthol, methyl ether and the phenyl-β-naphthylamide of 1-hydroxy-2-naphthoic acid there were similarly formed, together with the indamines, byproducts of a purple or dirty blue color. In this connection the dyes mentioned were carefully chromatographed on aluminum oxide or silica gel in benzene solution and afterwards crystallized. In the remaining cases, formation of a significant amount of side-product dyes was not observed.

In Table 1 are given the absorption maxima for the synthesized dyes in anhydrous methyl alcohol.

TABLE 1

R in formula (I)	λ_{max} (in mμ)	Absorption maximum shift (in mμ)	R in formula (I)	λ_{max} (in mμ)	Absorption maximum shift (in mμ)
H	608*	—	H	608	—
Cl	634	26	COOH	732	124
Br	638	30	$CONH_2$	672	64
$COOCH_3$	658	50	$CONHC_2H_5$	672	64
$COCH_3$	662	54	$CONHC_6H_5$	692	84
$CON(C_2H_5)_2$	638	30	CONH-α-$C_{10}H_7$	698	90
$CON(CH_3)C_6H_5$	640	32	CONH-β-$C_{10}H_7$	696	88
$CON(C_6H_5)_2$	645	37	$SO_2NHC_6H_5$	678	70
CON(C_6H_5)-α-$C_{10}H_7$	646	38	$SO_2N(C_2H_5)C_6H_5$	678	70
CON(C_6H_5)-β-$C_{10}H_7$	646	38	$SO_2N(C_6H_5)_2$	689	81

* In the synthesis of the N,N-dimethyl derivative of naphthol blue (λ_{max} in CH_3OH 588 mμ (cf. [1]), colored compounds are also formed by side reactions (λ_{max} of one of the dyes in CH_3OH 620 mμ.

The deep color of naphthol blue is evidently connected with the pronounced electron shift from the diethylamino groups along the conjugated chain to the carbonyl oxygen. Since the absorption maximum of this dye, as of the corresponding derivatives of phenol [11-13], moves into the short wave region on lowering the dielectric constant of the solvent (λ_{max} in CH_3OH 608 mμ, in C_4H_9OH 606 mμ, in C_6H_6 584 mμ), it may be supposed that in methanol solution the structure of naphthol blue is more correctly expressed by the covalent Formula (I), than by the inner salt (Ia) (cf [14-16]).

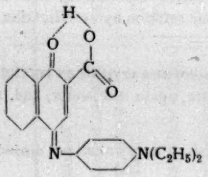
Thus the introduction into the 2-position of naphthol blue of electronegative substituents will evidently bring about an increase in electronic shift from the diethylamino groups along the conjugated chain, and consequently lead to a more uniform distribution of electron density in the chromophore, which, by analogy with other classes of dye [14], ought to bring about a deepening of color [5, 6, 11]. In addition, the magnitude of the bathochromic shift is evidently determined (within definite limits) by the degree of electronegativity of the substituent.*

* It should be noted that the presence of substituents in the conjugated chain of indamine dyes derived from α-naphthol may influence their color as a result of the purely auxochromic action of the substituent groups (the formation of a new positive or negative center). A clarification of this influence is possible only by studying the colors of the corresponding azaoxanines. Since the color of inner-salt dyes depends to a large degree on the uniformity of electron distribution in their fundamental chromophore, while the indamines studied by us contained substituents which are comparatively weak auxochromes, we did not take the purely auxochromic influence of the substituents in the 2-position of naphthol blue derivatives into account.

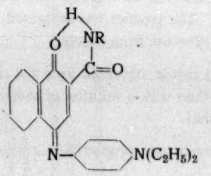
In fact, from the data in Table 1 it is clear that on the introduction into the 2-position of naphthol blue of an atom of chlorine or bromine, the absorption maxima of the dyes shift into the long wave region by 26 and 30 mμ respectively. The carbomethoxy group brings about a very large bathochromic effect (50 mμ), which is still increased slightly on its replacement by the acetyl group (54 mμ). The disubstituted carbamide group, as a result of its lower electronegativity, brings about a less pronounced deepening of color (bathochromic shift 30-38 mμ). Moreover, dyes with phenylalkylcarbamido and particularly with diphenyl and phenylnaphthylcarbamido groups are more deeply colored than the dye from the diethyl amide of 1-hydroxy-2-naphthoic acid, which is evidently connected with the electronegative character of the phenyl and naphthyl groups.

It has also been established that dyes containing free or substituted carbamido and more especially carboxyl groups show a markedly deeper color (a shift of 64-124 mμ) in spite of the fact that in electronegative character these substituents differ little from those considered above ($CONH_2$ or $CONHC_2H_5$ and $CON(C_2H_5)_2$; COOH and $COOCH_3$ [17]).

The group of dyes mentioned are distinguished by the presence in the substituent of a labile hydrogen atom, which may form an intramolecular hydrogen bond with the carbonyl oxygen (II and III):



(II)



(III)

The presence of hydrogen bonds in the above compounds was confirmed experimentally [18] by measurement of their infrared spectra.

An intramolecular hydrogen bond in a given instance should lead to an increase in electronic shift along the conjugated chain to the carbonyl oxygen i.e., to a greater uniformity of electron density and linkage in the chromophore of the dye, which will also produce a sudden deepening of color. Outside this group of dyes the influence of the degree of electronegativity of the substituent on the magnitude of the bathochromic shift of the absorption maximum is preserved. Thus, a dye with the COOH group is much more deeply colored than a $CONH_2$ derivative, while substitution of one of the hydrogen atoms of the carbamido group by an electronegative phenyl or naphthyl group leads to a marked deepening of color. Entry into the 2-position of naphthol blue of the electronegative phenylsulfamido group brings about a marked deepening in color (bathochromic shift 70 mμ). Replacement of an atom of hydrogen in the phenylsulfamido residue by the ethyl group does not affect the color of the dye, but the phenyl group brings about a fairly pronounced shift (11 mμ). Thus the presence of a labile hydrogen atom in the sulfamido group of these dyes does not lead to a deepening of color.

It should be noted that G D. Bagratishvili, D N. Shigorin and N. S. Spasokukotsky [18] have also shown, in the dye from the anilide of 1-naphthol-2-sulfonic acid, the presence of an absorption band characteristic of the hydrogen bond. The above authors consider that in their case there is more likely to be an intermolecular hydrogen bond between the sulfamido groups, whose formation does not affect the color of the dye.

The results presented agree with the conclusions made by us earlier [6,7]. In these papers, however, corrections should be made, in connection with the fact that the absorption maximum of naphthol blue (I, R = H) in ethyl alcohol lies at 607 mμ.

This and the following report are part of a more extended research work, begun on the initiative of Gleb Ivanovich Arbuzov, whose untimely death in 1950 ended his participation in the work.

EXPERIMENTAL

(In conjunction with Z. A. Simonyan and V. S. Ilyinskoi)

Amides of 1-hydroxy-2-naphthoic acid. Monosubstituted arylamides of 1-hydroxy-2-naphthoic acid were obtained by warming the corresponding amines at 135-170° with phenyl 1-hydroxy-2-naphthoate under reduced pressure (at first at 40-50 mm, afterwards at 15-30 mm). After removal of the phenol, the reaction products were purified by washing with water and alcohol (the anilide was, in addition, precipitated from alkaline solution by acid) and recrystallized from alcohol.

Disubstituted amides and the ethyl amide were obtained by action of the amines on 1-hydroxy-2-naphthoyl chloride in inert solvents; for the synthesis of the diaryl amides the reaction was carried out in dimethylaniline while in the remaining cases an excess of the original amine was used. The reaction was carried out at room temperature, except for the preparation of the diphenyl amide, which was carried out by warming on a boiling water bath. The reactant solutions were evaporated in vacuo, the residue was dried, washed with water, then with a 5% solution of sodium bicarbonate, again with water, and afterwards recrystallized from alcohol (the ethyl amide was in addition precipitated from alkaline solution by acid).

In the preparation of the diethyl amide the residue after evaporation of the reaction solution was extracted with ether, the ethereal solution was washed with a solution of sodium bicarbonate and extracted with a 5% solution of caustic soda. The product was separated from alkaline solution by acidification with acetic acid and purified by recrystallization from alcohol.

The methylphenyl amide, obtained from the reaction mixture as a crystalline precipitate, was filtered off, washed with water, then with a solution of sodium bicarbonate, again with water, and, after drying, was recrystallized from alcohol.

The preparation conditions, properties and results of analysis of the synthesized amides are given in Table 2.

1-Naphthol-2-sulfonyl chloride. To a suspension of 5.24 g potassium 1-naphthol-2-sulfonate, dried in vacuo at 100°, in 20 ml of anhydrous chloroform, 5.2 g of phosphorus pentachloride was added and the mixture heated on a boiling water bath for 1.5 hours. The reaction mass, after filtering, was evaporated in vacuo to small bulk. The precipitate obtained was filtered off and washed with benzene (b.p. 90-120°). Yield 3 g (61.8%). The product was purified by recrystallization from benzene (b.p. 90-120°). Yield 2.4 g (~50%). Colorless prisms from ligroin, m.p. 112-113°.

Found %: Cl 14.60 $C_{10}H_7O_3SCl$. Calculated %: Cl 14.61.

1-Naphthol-2-phenylsulfonamide. A solution of 2.42 g of 1-naphthol-2-sulfonyl chloride in 20 ml of anhydrous benzene was added gradually to a solution of 2.32 g aniline in 20 ml benzene. The precipitate obtained was filtered off, washed with 10 ml of benzene and water, dried, washed with a 5% solution of sodium bicarbonate, then with water, and, after drying, recrystallized from ethyl alcohol. Yield 2.11 g (70.5%). Colorless prisms (from ethyl alcohol). M.p. 148-149°.

Found %: N 4.77. $C_{16}H_{13}O_3NS$. Calculated %: N 4.67.

1-Naphthol-2-phenylethylsulfonamide. A solution of 2.42 g of 1-naphthol-2-sulfonyl chloride in 15 ml anhydrous benzene was added gradually to a solution of 3 g ethylaniline in 30 ml benzene. The precipitated ethylaniline hydrochloride was filtered off. The filtrate was washed with a 5% solution of sodium bicarbonate and then extracted with a 5% solution of caustic soda. The alkaline solution was acidified with acetic acid. The precipitate obtained was filtered off, washed with water, and, after drying, was recrystallized from alcohol. Yield 3.0 g (91.7%). Colorless prisms with m.p. 103°.

Found %: N 4.22. $C_{18}H_{17}O_3NS$. Calculated %: N 4.20.

1-Naphthol-2-diphenylsulfonamide. A solution of 1.21 g of 1-naphthol-2-sulfonyl chloride in 20 ml absolute ether was added to a solution of 0.84 g diphenylamine and 0.73 g dimethylaniline in 30 ml of absolute ether, after which the mixture was boiled in a flask with reflux condenser for 7 hours. The ethereal solution was then poured from the dimethylaniline hydrochloride and evaporated to dryness in vacuo. The residue was stirred up with water, the precipitate filtered off, washed with a 5% solution of sodium bicarbonate

TABLE 2

Amides of 1-hydroxy-2-naphthoic acid	Quantity of phenyl 1-hydroxy-2-naphthoate (A) or of 1-hydroxy-2-naphthoyl chloride (B) (in g)	Quantity of amine (in g)	Solvent and quantity used (in ml)	Reaction temperature	Time of heating (in hours)	Yield (%)	Appearance	Melting point	Analysis		
									N found (%)	Calculation	
										Formula	N (%)
Anilide	A, 5.28	3.72	—	125—145°	4	76	Colorless crystals	154°[8, 20]	—	—	—
α-Naphthylamide	A, 5.28	3.58	—	150—160	3	77.4	Colorless needles	162—163	4.40	$C_{21}H_{15}O_2N$	4.47
β-Naphthylamide	A, 10.56	7.16	—	160—170	3	89.5	Fine colorless prisms	181 (186[19])	4.20	$C_{21}H_{15}O_2N$	4.47
Amide	B, 3.09	0.68	Benzene, 280	20	1	99.2	Pale yellow needles	191—192 (190[9]) 202[8]	7.67	$C_{11}H_9O_2N$	7.48
Ethylamide	B, 8.24	4.5	Petroleum ether, 200; benzene, 20	20	1	32.5	Colorless prisms	152	6.36	$C_{13}H_{13}O_2N$	6.51
Diethylamide	B, 3.24	7.3	Petroleum ether, 220	20	1	25.7	Colorless prisms	57—58	5.99	$C_{15}H_{17}O_2N$	5.75
Methylanilide	B, 4.12	5.35	Petroleum ether, 100	20	1	61.7	Colorless prisms	136	4.88	$C_{18}H_{15}O_2N$	5.05
Diphenylamide	B, 2.06	1.69	Ether, 60•	35	3	79.6	Faintly yellow prisms	154	4.12	$C_{23}H_{17}O_2N$	4.12
Phenyl-α-naphthylamide	B, 3.45	3.6	Ether, 110••	20	12	83.1	Fine colorless prisms	161—162	3.60	$C_{27}H_{19}O_2N$	3.60
Phenyl-β-naphthylamide	B, 2.78	2.85	Ether, 85•••	20	12	87.8	Yellowish prisms	146—147	3.45	$C_{27}H_{19}O_2N$	3.60

• 1.5 g dimethylaniline.
•• 2.4 g dimethylaniline.
••• 2.0 g dimethylaniline.

TABLE 3

R in formula (I)	Quantity of α-naphthol or its derivative (in g)	Quantity of ethyl alcohol (in ml)	Solvent used for extraction	Solvent used for recrystallization	Yield of dye (%)		Appearance	Melting point	Analysis		
					Total	Pure material			N found (%)	Calculated	
										Formula	N (%)
Cl	1.06	30	Benzene	Ethanol	~100	68	Bronze needles	147°	8.43	$C_{20}H_{17}ON_2Cl$	8.27
Br	1.5	25	Benzene	Ethanol	91.3	52.2	Blue prisms	148—149	7.29	$C_{20}H_{17}ON_2Br$	7.31
COCH$_3$	0.93	30	Benzene	Methanol	~45*	30	Blue prisms shot with bronze	126	7.86	$C_{22}H_{20}O_2N_2$	8.08
COOH	0.94	30	Water	Propanol	~77	—	Ditto	172	7.95	$C_{21}H_{20}O_3N_2$	8.04
COOCH$_3$	1.01	25	Ethanol	Methanol	~28*	7	Ditto	105(157[3])	7.76	$C_{22}H_{22}O_3N_2$	7.73
CONH$_2$	0.93	50	Benzene	Ethanol	98	69.1	Bronze plates	204	11.98	$C_{21}H_{21}O_2N_3$	12.09
CONHC$_2$H$_5$	1.07	50	Benzene	Propanol	—	~60	Blue prisms shot with bronze	112	11.27	$C_{23}H_{23}O_2N_3$	11.19
CON(C$_2$H$_5$)$_2$	1.21	40	Benzene	Propanol	100	91	Bronze prisms	174	10.59	$C_{25}H_{29}O_2N_3$	10.41
CONHC$_6$H$_5$	1.31	75	Ethyl acetate	Ethyl acetate	86.2	40	Bronze needles	175—176	9.98	$C_{27}H_{23}O_2N_3$	9.92
CON(CH$_3$)C$_6$H$_5$**	1.38	85	Ether	Propanol	88	—	Greyish blue prisms	124	9.46	$C_{28}H_{27}O_2N_3$	9.60
CON(C$_6$H$_5$)$_2$**	1.69	50	Benzene	Propanol	95	—	Bronze plates	200	8.55	$C_{33}H_{29}O_2N_3$	8.41
CONH-α-C$_{10}$H$_7$***	1.56	20	Benzene	Ethyl acetate	90.9	26.4	Copper-red plates	194—195	8.76	$C_{31}H_{27}O_2N_3$	8.87
CONH-β-C$_{10}$H$_7$	1.56	25	Ethyl acetate	Ethyl acetate	76.6	—	Fine dark blue crystals	196—197	8.71	$C_{31}H_{27}O_2N_3$	8.87
CON(C$_6$H$_5$)-α-C$_{10}$H$_7$****	1.94	100	Benzene	Ethyl acetate	66.5	36.5	Fine blue prisms	221—222	7.86	$C_{37}H_{31}O_2N_3$	7.65
CON(C$_6$H$_5$)-β-C$_{10}$H$_7$*****	1.94	50	Benzene	Propanol	96.3	—	Dark blue crystals	167—169	7.38	$C_{37}H_{31}O_2N_3$	7.65
SO$_2$NHC$_6$H$_5$	1.5	40	Benzene	Propanol	98.7	—	Bronze plates	204	9.31	$C_{28}H_{25}O_3N_3S$	9.14
SO$_2$N(C$_2$H$_5$)C$_6$H$_5$	1.63	40	Benzene	Ethanol	70.8	—	Ditto	188—189	8.58	$C_{29}H_{29}O_3N_3S$	8.61
SO$_2$N(C$_6$H$_5$)$_2$	1.87	215	Benzene	Ethanol	90	73.7	Black prisms shot with bronze	181—182	7.65	$C_{32}H_{29}O_3N_3S$	7.84

*Yield quoted after chromatographing.

** Reaction mixture stirred for 1 hour.

*** Stirring continued for 2 hours.

**** Original amides dissolved in aqueous caustic soda and alcohol (1.5 g caustic soda and 50 ml water).

***** Reaction carried out in 250 ml benzene.

and with water, and, after drying, was recrystallized from ethyl alcohol. Yield 1.5 g (80%). Colorless prisms (from ethyl alcohol), m.p. 135°.

Found %: N 3.63. $C_{22}H_{17}O_3NS$. Calculated %: N 3.73.

Naphthol blue. This was obtained by the slightly modified method of Vittum and Brown [11], used by them for the synthesis of derivatives of phenol blue. To a suspension of silver chloride, obtained by mixing solutions of 7.47 g silver nitrate in 40 ml water and 2.92 g sodium chloride in 40 ml water, the following solutions were added in turn, with stirring: 3.2 g anhydrous sodium carbonate in 20 ml water, 0.72 g α-naphthol in 5 ml ethyl alcohol and 1.45 g diethyl-p-phenylenediamine sulphate in 40 ml water. After stirring the reaction mixture for 30 minutes, the precipitate of silver chloride and metallic silver with adsorbed dye was filtered off, washed with water, and after drying over calcium chloride was extracted with 200 ml benzene. The benzene solution was chromatographed on aluminum oxide. An orange-yellow impurity was first to be eluted from the column, followed by naphthol blue. The benzene solution was evaporated in vacuo and the residue (0.76 g, m.p. 109-116°) recrystallized from methanol. Yield 0.54 g (35.5%). Bronze prisms, m.p. 119-120°, which did not change on further purification.

Found %: N 3.63. $C_{22}H_{17}O_3NS$. Calculated %: N 3.73.

The blue dyes remaining on the column were eluted with a mixture of alcohol and chloroform. The solution was evaporated to dryness, and the residue (0.6 g) chromatographed on silica gel in benzene solution, after which two dyes were eluted in turn by benzene (No. 1: 0.13 g, bronze needles with m.p. 168-169°, λ_{max} in CH_3OH 635 mμ; No. 2 has not yet been separated in an analytically pure state), while a considerable quantity of blue-black material remained on the column.

On evaporation of the benzene solution obtained by extraction of the precipitate of silver chloride and metallic silver, and subsequent recrystallization of the residue (1.7 g) from propyl alcohol, dark blue crystals (m.p. 130-132°) separated, with an absorption maximum in C_2H_5OH of 625 mμ (found %: N 9.29).

Indamine dyes from the different derivatives of α-naphthol were prepared and separated as for naphthol blue. In the reaction with 2,4-dibromonaphthol a solution of sodium carbonate was added finally to the reaction mixture.

The dye from 1-hydroxy-2-naphthoic acid was obtained as the water-soluble sodium salt, which was extracted from the precipitate of silver chloride and metallic silver by water at ordinary temperature (on warming, the dye decomposes); the filtrate from the reaction was combined with the aqueous solution and the dye separated by acidification with CH_3COOH, after which it was purified by recrystallization.

The dyes from 2,4-dibromonaphthol, methyl ether, and the phenyl-β-naphthylamide of 1-hydroxy-2-naphthoic acid were purified by chromatography in benzene solution on aluminum oxide; the derivative of 2-acetylnaphth-1-ol, on silica gel. All the dyes were purified by recrystallization to constant melting point from suitable solvents.

The preparation conditions, properties and analysis results for the dyes synthesized are given in Table 3.

SUMMARY

1. Several new mono- and di-substituted amides of 1-hydroxy-2-naphthoic and 1-naphthol-2-sulfonic acids have been prepared.

A series of indamine dyes – derivatives of α-naphthol, containing different electronegative substituents in the 2-position has been synthesized and the absorption spectra in methyl alcohol have been studied.

2. It has been shown that entry of electronegative substituents into the 2-position of naphthol blue brings about a deepening of color; the magnitude of the bathochromic shift for the compounds studied depends on the degree of electronegativity of the substituent.

3. It has been established that indamine dyes – derivatives of α-naphthol containing in the 2-position a carboxyl or carbamido group with a labile hydrogen atom, have a particularly deep color, which is evidently connected with the formation of an intramolecular hydrogen bond between the substituent group and the carbonyl oxygen of the naphthalene nucleus.

LITERATURE CITED

[1] A. E. Porai-Koshits, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1945, 261.

[2] M. I. Krylova, Trans. Leningrad Chem. Tech. Inst. 11, 47 (1941).

[3] M. Pianka and H. C. Barany, J. Chem. Soc., 1948, 309.

[4] H. Schulze, Z. Naturforsch. 2, 400 (1947).

[5] P. W. Vittum and A. Weissberger, J. Photog. Sci. 2, 81 (1954).

[6] B. S. Portnaya, I. I. Levkoev and N. S. Spasokukotsky, Proc. Acad. Sci. USSR 82, 603 (1952).

[7] N. S. Spasokukotsky, I. I. Levkoev and B. S. Portnaya, Proc. Acad. Sci. USSR 93, 671 (1953).

[8] R. Anschütz and K. Runkel, Ann. 346, 361 (1906).

[9] H. Meyer, Monatsh. 22, 790 (1901).

[10] R. Anschütz, L. Hodenius, Ann. 415, 92 (1918).

[11] P. W. Vittum and G. H. Brown, J. Am. Chem. Soc. 68, 2235 (1946).

[12] L. G. S. Brooker and R. H. Sprague, J. Am. Chem. Soc. 63, 3214 (1941).

[13] P. W. Vittum and G. H. Brown, J. Am. Chem. Soc. 69, 152 (1947).

[14] I. I. Levkoev, N. N. Sveshnikov and E. B. Lifshits, Proc. Acad. Sci. USSR 74, 275 (1950).

[15] A. I. Kiprianov and V. S. Petrunkin, J. Gen. Chem. 10, 613 (1940).

[16] A. I. Kiprianov and E. S. Timoshenko, J. Gen. Chem. 17, 1468 (1947).

[17] A. I. Kiprianov and I. K. Ushenko, J. Gen. Chem. 15, 207 (1945).

[18] G. D. Bagratishvili, D. N. Shigorin and N. S. Spasokukotsky, J. Phys. Chem. 28, 2185 (1954).

[19] German Patent 441326 (1925).

[20] A. V. Kirsanov, E. S. Levchenko and G. S. Tretyakova, Ukrain. Chem. J. 19, 622 (1953).

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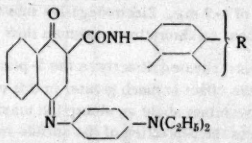
STUDIES IN THE FIELD OF AZOMETHINE DYES

II. INDAMINE DYES DERIVED FROM THE ANILIDE OF 1-HYDROXY-2-NAPHTHOIC ACID

N. F. Turitsina, B. S. Portnaya, N. S. Spasokukotsky, T. P. Bobkova, G. I. Arbuzov* and I. I. Levkoev

It has been shown earlier that the color of indamine dyes derived from naphthol blue is deepened by the introduction into the 2-position of the naphthalene nucleus of substituents of an electronegative nature [1,2] (see also [3]). The magnitude of the bathochromic shift of the absorption maximum of the of the dye depends on the degree of polarity of the substituent and on the possibility of formation of a hydrogen bond between this substituent and the carbonyl oxygen of the naphthalene nucleus [1,2]. Derivatives of alkyl and aryl amides of 1-hydroxy-2-naphthoic acid make up the largest group of dyes studied.

It seemedof interest to examine the influence on the color of these dyes of the presence in the anilide residue of substituents of different polarities. With this aim we synthesized dyes with structure (I) and studied their absorption spectra in methyl alcohol.



(I)

R = o-, m-, and p-CH_3, Cl, NO_2, NH_2, $N(CH_3)_2$, $NHCOCH_3$, p-$COCH_3$.

Of these dyes, the only one mentioned in the literature is that derived from the m-chloranilide of 1-hydroxy-2-naphthoic acid [4], which was, however, only obtained in a gelatine sheet by color development [5].

The dyes (I) were synthesized by us as in our previous work [2], by the oxidation with silver chloride of mixtures of the corresponding derivatives of α-naphthol and diethyl-p-phenylenediamine in alkaline aqueous alcohol solution, and were purified by recrystallization and in certain cases also by chromatography on aluminum oxide. The substituted anilides of 1-hydroxy-2-naphthoic acid necessary for the synthesis of the dyes are not, with the exception of the toluidides [6], described in the literature. The anilides with methyl, dimethylamino and nitro groups, and also those with chlorine atoms in the o-, m- and p-positions of the phenyl residue were obtained by warming (under reduced pressure) phenyl 1-hydroxy-2-naphthoate with the corresponding substituted anilines (see [2]). The amino and acetamino anilides were synthesized from the corresponding nitro derivatives by reduction with sodium hyposulfite and subsequent acetylation.

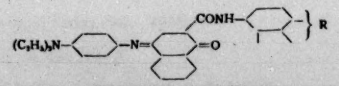
In the reduction, together with the aminoanilides soluble in benzene and toluene, there was formed a considerable quantity of a high-melting material, insoluble in these solvents, which has not yet been more closely studied. The p-acetylanilide of 1-hydroxy-2-naphthoic acid was synthesized by the reaction between p-aminoacetophenone and 1-hydroxy-2-naphthoyl chloride [2].

The positions of the light absorption maxima of the synthesized dyes in methyl alcohol are given in Table 1

* Deceased.

TABLE 1

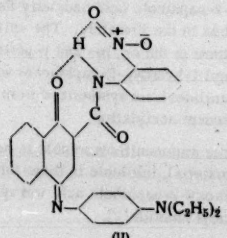
Positions of the Absorption Maxima of Methyl Alcohol Solutions of the Dyes:



Substituent R in the anilide residue	λ_{max} (in mμ)	Shift in absorption maximum (in mμ)	Substituent R in the anilide residue	λ_{max} (in mμ)	Shift in absorption maximum (in mμ)
H[2]	692	—	o-NHCOCH$_3$	692	0
o-N(CH$_3$)$_2$	687	−5	m-NHCOCH$_3$	693	+ 1
m-N(CH$_3$)$_2$	691	−1	p-NHCOCH$_3$	695	+ 3
p-N(CH$_3$)$_2$	690	−2	o-Cl	696	+ 4
o-NH$_2$	687	−5	m-Cl	697	+ 5
m-NH$_2$	691	−1	p-Cl	696	+ 4
p-NH$_2$	690	−2	o-NO$_2$	696	+ 4
o-CH$_3$	692	0	m-NO$_2$	698	+ 6
m-CH$_3$	691	−1	p-NO$_2$	705	+13
p-CH$_3$	691	−1	p-COCH$_3$	700	+ 8

In accordance with the ideas previously developed [2,3], it would be expected that the introduction into the anilide residue of the dye of electron-donating substituents should lighter the color, while the introduction of electron acceptors should deepen it. The data in Table 1 confirm these points. However, it should be pointed out that in any given instance the introduction of a substituent differing sharply in character shows a comparatively small effect. A particularly slight influence is shown by electropositive substituents, for example amino and dimethylamino groups, which (with the exception of the ortho-isomers) bring about an absorption maximum shift, into the short-wave region, of the order of 1-2 mμ. Electronegative substituents exert a more noticeable influence: the presence of the nitro group brings about an absorption maximum shift of up to 13 mμ into the long-wave region.

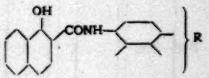
If the effect of the same substituents, situated directly in the 2-position of the naphthalene nucleus (see [2]) is taken for comparison, it is seen that the effect is much greater in this case. Thus, the introduction of the acetyl group into the 2-position of naphthol blue brings about an absorption maximum shift of 54 mμ into the long wave region, while entry of the same group into the p-position of the anilide residue of the dye with structure (I) brings about a bathochromic shift of only 8 mμ. A similar difference is observed in a comparison of the dyes containing a substituent chlorine atom. The noticeably smaller influence of substituents in the anilide residue is evidently connected with the fact that they act only indirectly on the fundamental chromophoric system of the dye, by influencing the amide nitrogen in one or other direction. In this connection substituents in the ortho position, being nearest, should show the greatest effect. This is confirmed by the o-amino and o-dimethylamino derivatives. Other features are observed in the case of the nitro derivatives. The oxygen atom of the o-nitro group, like the o-carboxy group [7], can, as a result of steric effects, form a hydrogen bond with the amido group, as a result of which the hydrogen bond between the latter and the carbonyl oxygen in the naphthalene nucleus is evidently weakened [formula (II)].



(II)

TABLE 2

Preparation Conditions and Properties of Some Substituted Anilides of 1-Hydroxy-2-Naphthoic Acid



R	Excess amine (%)	Time of heating (in hours)	Method of separation	Yield of product (% of theoretical)		Appearance	Solvent used for recrystallization	Melting point	Analysis		
				Unpurified	Pure				Found N (%)	Calculated: Formula	Calculated: N (%)
o-CH_3[6]	—	4	A	70	64	Colorless needles	Ethyl alcohol	110--111° (89—90[6])	5.21	$C_{18}H_{15}O_2N$	5.05
m-CH_3[6]	—	4	"	90	—	Ditto	Ditto	124—126 (118[6])	5.26	$C_{18}H_{15}O_2N$	5.05
p-CH_3[6]	—	4	"	92	—	Colorless prisms	"	154—155 (155—156[6])	5.26	$C_{18}H_{15}O_2N$	5.05
o-$N(CH_3)_2$	20	1—2	B	78	—	Ditto	"	110—111	9.11	$C_{19}H_{18}O_2N_2$	9.15
m-$N(CH_3)_2$	20	1—2	B	87	64	Colorless plates	Toluene	173	8.99	$C_{19}H_{18}O_2N_2$	9.15
p-$N(CH_3)_2$	•	1—2	B	69	50	Greenish yellow prisms	Ditto	173—174	9.17	$C_{19}H_{18}O_2N_2$	9.15
o-Cl	50	3	A	88	—	Colorless needles	Ethyl alcohol	160—162	4.68	$C_{17}H_{12}O_2NCl$	4.70
m-Cl	50	1	A	85	—	Ditto	Ditto	179—180	4.73	$C_{17}H_{12}O_2NCl$	4.70
p-Cl	50	3	A	88	—	Colorless prisms	"	172—173	4.81	$C_{17}H_{12}O_2NCl$	4.70
o-NO_2	—	1—2	C	79	60	Long bright yellow rectangular prisms	Acetic acid	200—201	8.98	$C_{17}H_{12}O_4N_2$	9.09
m-NO_2	—	1—2	C	74	—	Ditto	Ditto	242	9.07	$C_{17}H_{12}O_4N_2$	9.09
p-NO_2	25	3	C	93	74	Yellow prisms	"	241	9.00	$C_{17}H_{12}O_4N_2$	9.09

• 20 % excess of ester taken.

TABLE 3
Preparation Conditions and Properties of the Dyes (I)

R	Quantity of ethyl alcohol in reaction mixture (ml)	Solvent used for recrystallization	Yield of product (as % theoretical)		Melting point	Appearance	Analysis		
			Unpurified	Pure			N found (%)	Calculated	
								Formula	N (%)
o-$N(CH_3)_2$*	—**	Propanol	75	52	159—160°	Reddish violet plates	11.76, 11.71	$C_{29}H_{30}O_2N_4$	12.02
m-$N(CH_3)_2$*	—**	Ditto	66	25	154—155	Fine dark blue prisms	11.75	$C_{29}H_{30}O_2N_4$	12.02
p-$N(CH_3)_2$	2.5	Benzene	89	39	205—206	Fine dark blue prisms	12.24	$C_{29}H_{30}O_2N_4$	12.02
o-NH_2	—	Propanol	67	21	192—193	Lustrous copper-red needles	12.82	$C_{27}H_{26}O_2N_4$	12.78
m-NH_2	20	Ditto	95	37	178—179	Circular brownish violet leaflets	12.48	$C_{27}H_{26}O_2N_4$	12.78
p-NH_2***	20	"	80	—	231—232	Dark green crystals	13.00	$C_{27}H_{26}O_2N_4$	12.78
o-$NHCOCH_3$*	5	Ethyl acetate	93	70	201—202	Lustrous violet needles	11.81, 11.85	$C_{29}H_{28}O_3N_4$	11.67
-NHCOCH*	4	Benzene	59	56	208—209	Fine blue needles with violet luster	11.90	$C_{29}H_{28}O_3N_4$	11—67

p-$NHCOCH_3$**	6	Ditto	10	2	209—210	Light fine bright blue needles	11.40	$C_{29}H_{28}O_3N_4$	11.67
o-CH_3	15	Propanol	80	69	180—180.5	Greyish blue needles	9.69 9.75	$C_{28}H_{27}O_2N_3$	9.79
m-CH_3	15	Ditto	96	65	185—186	Lustrous bronze prisms	9.50, 9.66	$C_{28}H_{27}O_2N_3$	9.79
p-CH_3	15	"	79	60	194—195	Lustrous bronze plates	9.77	$C_{28}H_{27}O_2N_3$	9.79
o-Cl	30	"	92	68	183—184	Greenish blue needles with bronze luster	9.37	$C_{27}H_{24}O_2N_3Cl$	9.16
m-Cl	30	"	—	72	183—185	Dark blue prisms shot with gold	9.37	$C_{27}H_{24}O_2N_3Cl$	9.16
p-Cl	30	"	86	64	197—197.5	Fine blue-violet needles	9.42	$C_{27}H_{24}O_2N_3Cl$	9.16
o-NO_2	5	Ethyl acetate	97	42	208—209	Lustrous green needles	12.16	$C_{27}H_{24}O_4N_4$	11.96
m-NO_2***	3	Ditto	—	7	195—196	Red-violet square prisms with crimson luster	12.00	$C_{27}H_{24}O_4N_4$	11.96
p-NO_2*	—	"	47	32	211—212	Lustrous bright green plates	12.10, 11.98	$C_{27}H_{24}O_4N_4$	11.96
p-$COCH_3$	30	Propanol	82	54	185—186	Blue prisms shot with bronze	9.38	$C_{29}H_{27}O_3N_3$	9.03

* Dye extracted from reaction mass with ethyl acetate.

** 0.6 g caustic soda added to reaction mixture instead of sodium carbonate.

*** Dye chromatographed in benzene solution on aluminum oxide before recrystallation.

As a result, the bathochromic effect of this hydrogen bond, characteristic of dyes from unsubstituted or monosubstituted 1-hydroxy-2-naphthoic amides (see [1,2]), is somewhat suppressed, and this evidently also explains the smaller effect on color of the nitro group in the ortho position. The greater effect of the nitro group in the para position may be connected with conjugation with the amide nitrogen, which is not possible for the meta derivative. The remaining substituents occupy an intermediate position, with reference to their electronic properties, between the amino and nitro groups, and exert a corresponding influence on the color.

EXPERIMENTAL*

Substituted anilides of 1-hydroxy-2-naphthoic acid (from the phenyl ester of this acid). A finely ground mixture of 0.02 mole of phenyl 1-hydroxy-2-naphthoate and 0.02-0.03 mole of the substituted aniline were warmed in a Claisen flask on an oil bath at 140-170° (in the bath) for 1-4 hours, at a residual pressure of normally 40-60 mm initially, and 20 mm finally. The phenol or mixture of phenol and excess amine was then slowly distilled off. The mass obtained was treated by one of the methods described below (A, B or C).

A. Steam was passed through the reaction mixture to separate the phenol, after which a solution of caustic soda (0.5-3 g in a small volume of water) was added, and the mixture heated until the product dissolved. The solution was filtered, cooled, and acidified with dilute hydrochloric or acetic acid. The crystals obtained were separated, washed with water, and dried.

B. The mass was ground thoroughly, in the cold or with warming, with a small quantity of ethyl alcohol. The crystalline anilide was filtered off, washed with alcohol and dried.

C. The reaction mass was treated with glacial acetic acid at the boil, the crystalline anilide filtered off after cooling and washed with ether.

The anilides obtained were purified in each case by recrystallization to constant melting point from suitable solvents. The synthesis conditons, properties and analysis results for the anilides obtained are given in Table 2.

o-Amino anilide of 1-hydroxy-2-naphthoic acid. 9 g of the o-nitranilide of 1-hydroxy-2-naphthoic acid was dissolved in a 20% solution of caustic soda (90 ml), the sqlution was diluted with water (800 ml), and a solution of 42 g sodium hyposulfite in 150 ml water was added gradually with stirring at 80-90°. The solution was then boiled for 10 minutes, cooled, filtered and acidified with acetic acid. The colorless crystals obtained were separated, washed with water and dried. Weight 4.75 g, m.p. 190-193°. The o-amino anilide was extracted from the reaction product by boiling with toluene. Yield 1.57 g (23.5%). Colorless needles (from toluene). M.p. 217-218°. Insoluble in water, soluble with difficulty in toluene and ether, easily soluble in alcohol and 5% caustic soda solution.

Found %: N 10.21, 10.16. $C_{17}H_{14}O_2N_2$. Calculated %: N 10.07.

After extraction of the reaction product with toluene, a considerable residue was left, which did not melt below 260°. This product has not been further studied.

m-Amino anilide of 1-hydroxy-2-naphthoic acid. This was obtained in the same way as the o-derivative. In this case 66 g sodium hyposulfite in 280 ml water was added at 65° and the mixture boiled for 3-4 minutes. The m-amino anilide was extracted from the reaction product with boiling benzene (b.p. 100-120°). Yield 35.3%. Thin slightly yellow transparent plates (from benzene). M. p. 189-190°. Soluble with difficulty in ether and water, more readily in benzene, yet more readily in ethyl alcohol.

Found %: N 9.98. $C_{17}H_{14}O_2N_2$. Calculated %: N 10.07.

The residue, insoluble in benzene, melted at 240-241°.

p-Amino anilide of 1-hydroxy-2-naphthoic acid. This was obtained similarly to the o- and m-amino anilides, from the p-nitranilide. The hyposulfite (48 g in 170 ml water) was added at 65° over a period of 15 minutes; after which the mixture was stirred at the same temperature for a further 5 minutes. The yield of unpurified p-amino anilide was 95.9%, that of the recrystallized material 70%. Thin flakes (from toluene). M. p. 189°. Insoluble in water and ether, readily soluble in toluene and alcohol, and in 5% caustic soda solution.

* With V. S. Ilyinskoi.

Found %: N 9.90, 9.98. $C_{17}H_{14}O_2N_2$. Calculated %: N 10.07.

After crystallization of the reaction product from toluene, a residue, melting at 279-280°, remained.

o-Acetamino anilide of 1-hydroxy-2-naphthoic acid. A solution of 2.78 g of the o-amino anilide in glacial acetic acid (25 ml) was boiled with 1.1 g acetic anhydride for 6 hours. After cooling, the liquid was diluted with 300 ml of 5% caustic soda solution, filtered and acidified with acetic acid. Yield 96.9%. Fine needles (from 80% ethyl alcohol). M. p. 214-215°. On mixing with the original o-aminoanilide, the melting point was depressed. Rreadily soluble in alcohol and 5% caustic soda solution, soluble with difficulty in toluene, ether and benzene, insoluble in water.

Found %: N 8.63. $C_{19}H_{16}O_3N_2$. Calculated %: N 8.75.

m-Acetamino anilide of 1-hydroxy-2-naphthoic acid. A solution of 2.78 g of the m-amino anilide in glacial acetic acid (15 ml) was boiled with 1.5 g acetic anhydride for 3 hours. Greyish crystals separated from the cooled solution and were filtered off and washed with benzene. Yield 84.7%. Fine colorless needles (from ethyl alcohol). M. p. 221-222°. Readily soluble in benzene, less readily in alcohol, sparingly soluble in water.

Found %: N 8.47, 8.53. $C_{15}H_{16}O_3N_2$. Calculated %: N 8.75.

p-Acetamino anilide of 1-hydroxy-2-naphthoic acid. This was obtained similarly to the m-acetamino anilide of 1-hydroxy-2-naphthoic acid. It was separated from the reaction solution as for the o-derivative. Yield 90.3%. Colorless needles (from a mixture of 2 parts toluene and 1 part ethyl alcohol). M. p. 254-255°. Readily soluble in acetic acid, 5% caustic soda solution and ethyl alcohol, sparingly soluble in toluene and ether.

Found %: N 8.65. $C_{19}H_{16}O_3N_2$. Calculated %: N 8.75.

p-Acetylanilide of 1-hydroxy-2-naphthoic acid. A solution of 2.06 g 1-hydroxy-2-naphthoyl chloride in 20 ml anhydrous benzene was added to a solution of 1.35 g p-aminoacetophenone in 20 ml anhydrous benzene, containing 1.82 g dimethylaniline. The mixture was warmed for 4 hours on a boiling water bath. 20 ml of 20% sodium carbonate solution was added to the reaction mass; the dimethylaniline and benzene were steam-distilled and the solution obtained was acidified with dilute (1:1) hydrochloric acid.

The precipitate which separated was filtered off, washed with water, ground up with 50 ml 10% sodium bicarbonate solution, again filtered off, washed with water and dried. Yield 80.2%. Colorless needles (from ethyl alcohol). M.p. 194-195°. Soluble with some difficulty in ethyl alcohol.

Found %: N 4.83. $C_{19}H_{15}O_3N$. Calculated %: N 4.59.

Preparation of the indamine dyes. The dyes were obtained by the oxidation with silver chloride of a mixture of diethyl-p-phenylenediamine and the substituted anilide of 1-hydroxy-2-naphthoic acid (0.001 mole) in alkaline aqueous alcohol solution (see [2]). The mixture was stirred in most cases for 30 minutes; in the case of the nitro and dimethylaminoanilides, for 1 hour. The unstable crystals from the amino anilides were obtained by shaking up the reaction mixture with benzene (50 ml) for 30 minutes. The mixture was then diluted with benzene, the precipitate filtered off, the benzene layer separated from the aqueous layer, washed with water and the benzene distilled off in vacuo. Separation of the other dyes was carried out as described in our previous work [2]. All the dyes were purified by recrystallization. In some cases a preliminary chromatographic separation on aluminum oxide was carried out. The preparation conditions and properties of the dyes synthesized, and their analysis results, are given in Table 3.

SUMMARY

1. A series of dyes derived from the anilide of 1-hydroxy-2-naphthoic acid, with substituents of widely varying electronic character in the anilide residue, has been synthesized; the absorption spectra of their solutions in methyl alcohol have been measured.

2. It has been shown that introduction of substituents into the anilide residue has, in general, little effect on the color of the dye. Electropositive groups bring about a slight hypsochromic shift of the absorption maximum, while electronegative groups brings about a bathochromic shift. The effect of electronegative substituents is more marked than that of electropositive substituents.

3. It has been observed that a nitro group in the ortho position of the anilide residue exerted less influence on color than in the meta and para positions. The explanation proposed is that this phenomenon is connected with the formation of a hydrogen bond between the amide groups and the oxygen atom of the o-nitro group.

LITERATURE CITED

[1] B. S. Portnaya, I. I. Levkoev and N. S. Spasokukotsky, Proc. Acad. Sci. USSR 82, 603 (1952).

[2] B. S. Portnaya et al., J. Gen. Chem. 26, 2537 (1956) (T.p. 2831).*

[3] P. W. Vittum and A. Weissberger, J. Photog. Sci. 2, 81 (1954).

[4] H. Schulze, Z. Naturforsch. 28, 400 (1947).

[5] A. Weissberger and H. Porter, J. Am. Chem. Soc. 65, 1495 (1943).

[6] G. V. Jadhav, S. N. Rao, N. V. Hirwe, J. Univ. Bombay 5, 137 (1936); Chem. Abs. 31, 46649 (1937).

[7] N. S. Spasokukotsky, I. I. Levkoev and B. S. Portnaya, Proc. Acad. Sci. USSR 93, 671 (1953).

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* T. p = C. B. Translation pagination.

THE REACTION BETWEEN GLYCINE AND PHOSPHOMOLYBDIC ACID

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Phosphotungstic acid gives a series of sparingly soluble compounds with diaminoacids and other nitrogen-containing bases [1]. This enables it to be used for the quantitative determination of these compounds. We undertook to examine the possibility of using phosphomolybdic acid for the same purpose. Special interest was also attached to the degree of replacement in the salts obtained, since the heteropolyacids of tungsten and molybdenum are polybasic [2]. There are no data in the literature on the use of phosphomolybdic acid as a precipitant for aminoacids.

Synthesis of the compounds of glycine with phosphomolybdic acid was carried out in aqueous and in aqueous alcohol media. To obtain salts with different degrees of replacement, the calculated amounts of aqueous 0.5 M glycine solution were added to an aqueous 0.5 M solution of phosphomolybdic acid. To check the effect of a large excess of glycine, a specimen was prepared by the reaction of 12 equivalents of glycine with phosphomolybdic acid. Later, 2 syntheses were carried out in aqueous alcohol medium, using an aqueous solution of glycine and an alcoholic solution of phosphomolybdic acid (Table 1).

TABLE 1

Synthesis Conditions

Specimen No.	Calculated degree of replacement in the salt	Phosphomolybdic acid taken		Milliliters of glycine solution, containing 0.047 g in 1 ml		Color of compounds obtained
		Aqueous soln.				
1	1	2.58		2		
2	2	2.58		4		White precipitates; green solutions
3	3	2.58		6		
4	4	2.58		8		
5	5	2.58	Grams in 10 ml water	10		
6	6	2.58		12		White precipitates; pale bluish solutions
7	7	2.58		14		
8	7	2.58*		14		
9	Excess (12 equiv. glycine)	2.58		24		
		In aqueous alcohol medium				
10	3.5 Equiv. glycine	18.61	Grams in 50 ml ethyl alcohol	2.25	Grams in 20 ml water	White precipitates; green solutions
11	3 Equiv. glycine	18.61		2.00		

* With addition of 5 ml ethyl alcohol.

The white color of precipitates 1-3 appeared only after washing with water (before washing the precipitates were an intense yellow). The size of the crystals varied, but did not exceed 0.5 mm. Specimens 1 and 2 consisted of well-distinguished comparatively coarse crystals and were easily separated from the solution, but specimens 6, 7 and 9 gave a suspension which settled with difficulty. Crystals were not visible in it and filtration through a Scott crucible was slow. It was obvious that in these cases molybdic acid, formed by decomposition of the heteropolyanion, was present as well as the glycine compound. Precipitates 3-5 possessed intermediate properties; specimen 8 filtered particularly slowly due to the presence of colloidal molybdic acid.

In the aqueous alcohol medium, crystalline precipitates were obtained which appeared yellow before washing with alcohol. The specimens turned faintly pink on exposure to light. The color became more pronounced on exposure to direct sunlight.

Analysis of the specimens was carried out as follows: 1) drying to constant weight at 110-130° of samples taken simultaneously; 2) determination of residue after ignition; 3) P_2O_5 determination; 4) Kjeldahl determination of ammonia. Water was determined by difference after conversion of the ammonia to glycine.

Ignition was begun at a temperature of 110-130°, which was then gradually raised to 300-350° to burn off almost all the organic material. Further ignition in a muffle at 400-600° gave a loss in weight of no more than 0.5 - 0.7%. No MoO_3 deposit was noticed on the walls or roof of the crucible during ignition. The temperature during the ignition was followed using a thermometer and thermocouple. The ignition results are given in Table 2.

TABLE 2

Residues After Ignition

Specimen No.	Weight of dry sample (g)	Residues	
		Weight (g)	Percentage of dry weight
1	0.2610	0.1994	76.41
2	0.4127	0.3143	76.16
3	0.3953	0.2990	75.89
4	0.5173	0.3953	75.90
5	0.5592	0.4268	76.31
6	0.8745	0.6620	75.71
7	0.7794	0.5907	75.80
9	0.6705	0.5034	75.07
			Average 75.85%
10	0.2700	0.1875	69.4
11	0.9754	0.6725	68.9
			Average 69.15%

P_2O_5 was precipitated as NH_4MgPO_4, by Rosenheim's method [3]. The analysis results are given in Table 3. Specimens 10 and 11 gave no precipitate with magnesia mixture.

TABLE 3

P_2O_5 Content

Specimen No.	Weight of sample (g)	Weight of $Mg_2P_2O_7$ obtained after ignition (in g)	P_2O_5	
			(in g)	Percentage of sample weight
3	0.4892	0.0038	0.0023	0.47
4	0.4407	0.0040	0.0024	0.55
5	0.6633	0.0057	0.0035	0.52
8	0.8101	0.0075	0.0046	0.56

For the determination of nitrogen the specimens were decomposed with sulfuric acid by heating with small quantities of copper sulfate and potassium sulfate; the solution became fully transparent only after 50-100 hours. Its color was slightly yellow; there was no precipitate of H_2MoO_4. Hausmann [4], who decomposed phosphotungstic amino-acids by a similar method, always obtained a yellow precipitate, evidently H_2WO_4, towards the end of the decomposition. Data on the ammonia content of the specimens obtained from aqueous solutions are given in Table 4.

As is seen from the data in the tables given above, all the syntheses in aqueous media, using different numbers of equivalents of glycine, gave products with identical values of ammonia, phosphorus and incombustible residue content. From this it may be concluded that the same compound is produced in every case. The amount of P_2O_5 is small, and it may be considered as an accidential impurity. The figures given may be made more precise by making corrections for the P_2O_5:

$$\% MoO_3 = \frac{\% \text{ residue} - \% P_2O_5}{100 - \% P_2O_5}; \quad \% NH_3 = \frac{NH_3 \text{ found}}{100 - \% P_2O_5} \text{ and}$$

$$\% H_2O = 100 - \% MoO_3 - \% \text{ glycine}.$$

TABLE 4

Ammonia and Glycine Content

Specimen No.	Dry weight of samples (in g)	NH_3 obtained (in g)	NH_3 (%)
3	0.3587	0.0152	4.23
5	0.6737	0.0300	4.45
6	0.6133	0.0270	4.40
9	0.5897	0.0275	4.66
		Mean; 4.44 (converted to glycine 19.53%)	

The mean figures obtained in this way are given in Table 5.

Thus the compound formed in aqueous medium is close to glycine tetramolybdate:

$$\left(\begin{matrix} CH_2COOH \\ | \\ NH_3^+ \end{matrix}\right)_3 O(MoO_3)_4.$$

The specimen did not lose all its water of crystallization on drying; thus the ratio % MoO_3: % CH_2NH_2COOH shows particularly clearly the identity of the specimen with glycine tetramolybdate.

The structural formula of the tetramolbydates $R_6H_4[H_2(Mo_2O_7)_6]$ [5] allows them to be considered as heteropoly compounds with complex-forming hydrogen. Our research confirms that the compound obtained has indeed the coordination formula given above, which gives the calculated values (%): CH_2NH_2COOH 19.7, MoO_3 75.57, H_2O 4.73, ratio MoO_3: CH_2NH_2COOH 3.82.

$$\left(\begin{matrix} CH_2COOH \\ | \\ NH_3 \end{matrix}\right)_6 H_4[H_2(Mo_2O_7)_6],$$

TABLE 5

Composition of Specimens 1-7 and 9 Obtained in Aqueous Medium

	MoO_3 (%)	CH_2NH_2COOH (%)	H_2O (%)	Ratio MoO_3 : CH_2NH_2COOH
Found (mean)	75.71	19.63	4.66	3.86
Calculated:				
for glycine tetramolybdate	77.09	20.18	2.73	3.82
for glycine trimolybdate	71.94	25.02	3.04	3.62

E. A. Nikitina [6] has shown that in the decomposition of phosphomolybdates, corresponding paramolybdates of composition $R_5H_5[H_2(MoO_4)_6]$, are formed; silicomolybdates form trimolybdates with coordination formula $R_4H_6[H_2(MoO_4)_6]$. Thus in aqueous medium the decomposition of heteropolymolybdic acids with complex-forming silicon and phosphorus leads to the formation of more simple heteropolyacids with a central coordinating H_2 group, i.e., to para-, tri- and tetra-molybdates.

In aqueous alcohol medium a product is obtained whose composition does not correspond to any polymolybdate: in this case a mixture of different polymolybdates is evidently formed.

An attempt was made to block the glycine amino group with formalin in the hope that this would reduce the

destructive action of the glycine on the phosphomolybdic acid. This was not successful. A pale yellow precipitate was obtained, which became white on washing. The excess of formalin in the solution exerted a powerful reducing effect on the phosphomolybdic acid used for the precipitation. Analogous results were obtained using urotropine and urea in place of glycine; white precipitates were obtained.

We have to thank Professor E. A. Nikitina for suggesting the research topic and for assistance during the work.

SUMMARY

1. The reaction between glycine and phosphomolybdic acid has been studied in aqueous and in aqueous alcohol media.

2. It has been shown that in aqueous medium the complex decomposes with the formation of sparingly soluble precipitates of glycine tetramolybdates. Research has confirmed the coordination formula of the tetramolybdates. Part of the phosphoric acid formed is adsorbed by the precipitate.

3. Blocking of the glycine amino group with formalin does not lessen the destructive effect of the glycine on the complex in aqueous medium.

4. In aqueous alcohol medium a mixture of different polymolybdates is formed.

LITERATURE CITED

[1] W. Gulewitsch, Z. physiol. Chem. 27, 178 (1899); E. Drechsel, Arch. Anat. u. Physiol. 25, 4 (1891); R. Block, D. Bolling, The Amino Acid Composition of Proteins and Foods (N. Y., 1947); A. Kossel, Z. physiol. Chem. 31, 215 (1900/01); H. Wu, J. biol. Chem. 43, 189 (1920); E. Winterstein, Z. physiol. Chem. 34, 153 (1901); Van Slyke, J. biol. Chem. 156, 713 (1944), 22, 281 (1915); 23, 411 (1915); 10, 15 (1911/12); 146, 137 (1942).

[2] E. A. Nikitina, J. Appl. Chem. (USSR) 7, 1194 (1937), Progr. Chem. 8, 831 (1939); J. Gen. Chem. 10, 780 (1940).

[3] Rosenheim and Janiche, Z. allgem. anorg. Chem. 101, 215 (1917).

[4] W. Hausmann, Z. physiol. Chem. 27, 95 (1899).

[5] Mellor, A. Comprehensive Treatise on Inorganic Chemistry (1943), 11, 582.

[6] E. A. Nikitina, J. Gen. Chem. 10, 997 (1940); 22, 1085 (1952).

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THE HYDROLYSIS OF THE POLYANHYDRIDES OF ADIPIC AND SEBACIC ACIDS

M. S. Dudkin and E. M. Goldstein

On warming dibasic acids with six or more carbon atoms in the chain with acetic anhydride, linear polymers, the so-called α-polyanhydrides [1-4], are formed. Their molecular weight is approximately equal to 5000 [2]. Further heating of the α-polyanhydrides leads to the formation of superpolyanhydrides or ω-polyanhydrides, which can be drawn out into threads forming lustrous fibers. The disadvantage of these fibers is their easy hydrolysis. Hill [1-4], without giving giving quantitative data, considers that the polyanhydrides are hydrolyzed back to the original acid molecules under the influence of both boiling and cold water.

The object of our work was to characterize quantitatively the hydrolysis of adipic and sebacic α-polyanhydrides, which, to our knowledge, has not been described in the literature.

Adipic and sebacic α-polyanhydrides obtained by Hill's method [1,2], were hydrolysed. The determination of molecular weight was carried out by the end-group method worked out by Hill for these compounds [2]. The influence of atmospheric moisture and of aqueous and alkaline media at different temperatures on the polyanhydride decomposition was studied. Hydrolysis by atmospheric moisture was followed by the change in melting point of the polyanhydride, since change in the chain length of a high-molecular weight compound brings about a change in its melting point [5,6].

Atmospheric moisture hydrolyses the polyanhydrides in different ways (Table 1). Adipic polyanhydride is almost completely hydrolysed to adipic acid in 25 days, while sebacic acid is practically unchanged. This property must be considered when the polyanhydrides are being stored.

TABLE 1

Relation Between Hydrolysis of Adipic Polyanhydride by Atmospheric Moisture and Time.

Time (in days)	Melting point of polyanhydride
0	71°
4	105
7	123
10	131
12	137
14	138
21	139
24	140

The extent of decomposition of the polyanhydrides in aqueous and alkaline media was determined by the amount of free acid formed in the hydrolysis and passing into solution. The nature of polyanhydride decomposition in aqueous medium is different (Table 2). Adipic acid is hydrolysed initially at a considerable rate, while the opposite behavior is shown by sebacic polyanhydride. This difference may be explained by the different solubility in water of the initial decomposition products of the polyanhydrides. The compounds formed initially in hydrolysis of adipic polyanhydride are probably characterized by a greater solubility (compared with sebacic anhydride), which thus causes the considerable increase in acid titer in the initial period of the hydrolysis. The decomposition process of the polyanhydrides is accelerated by hydroxyl ions and by warming (Tables 2 and 3). The hydrolysis of sebacic polyanhydride in alkaline medium is characterized by a first-order equation.

EXPERIMENTAL

Preparation of adipic and sebacic α-polyanhydrides [1,2]. 20 g of adipic (sebacic) acid, recrystallized from ethyl alcohol, and 80 ml of freshly distilled acetic anhydride were warmed in a flask with reflux condenser at the boil for 6 hours. Volatile products were distilled off in vacuo on a water bath. The crude polyanhydride was dissolved in boiling benzene and precipitated with petroleum ether. It was dried in vacuo over caustic potash, phosphorus

pentoxide and paraffin. The polyanhydrides obtained appeared as white fine crystalline powders. M. p. adipic polyanhydride 71°, Mol. wt. 4540; M. p. sebacic polyanhydride 79°, Mol. wt. 5240.

Hydrolysis by atmospheric moisture. The polyanhydride was finely ground and placed in a thin layer on a watch glass. The melting point of the material, which was exposed to the atmosphere (humidity 65-72%), was determined after definite intervals (Table 1). The product remaining after this experiment was warmed with water, recrystallized, and its melting point again determined. For the adipic polyanhydride decomposition product this was 151°, and for that of sebacic polyanhydride 134°, i.e., it indicated the formation of the free acids.

TABLE 2

Polyanhydride Hydrolysis in Aqueous Medium

Time (in minutes)	Adipic polyanhydride			Sebacic polyanhydride		
	29°	39°	49°	70°	80°	90°
	Acid titer			Acid titer		
5	117.1	129.8	122.1	—	—	—
15	148.1	156.6	162.4	1.8	3.1	8.3
30	163.2	175.9	197.0	9.4	18.0	71.2
45	171.9	181.8	207.9	17.9	91.3	271.7
60	174.0	190.5	237.2	35.3	229.6	500.4
75	—	—	—	62.1	505.5	—

TABLE 3

Hydrolysis of Sebacic Polyanhydride in Alkaline Medium

Time (in minutes)	Acid titer			$K = \frac{2.303}{t} \log \frac{C_A}{C_A - C_x}$	
	22°	32°	42°	22°	42°
15	40.2	81.0	93.2	0.0049	0.0122
30	64.5	127.1	193.3	0.0041	0.0142
45	96.8	150.7	212.8	0.0043	0.0107
60	109.1	185.3	256.6	0.0037	0.0103
75	159.4	195.0	265.6	0.0045	0.0087
			Mean value of K	0.0043	0.0115

Hydrolysis in aqueous medium. A three-necked flask fitted with stirrer and thermometer, and containing 200 ml water, was placed in a thermostat. After warming the water to the required temperature, a sample of the polyanhydride (1.468 g for the adipic polyanhydride, 0.2126 g for sebacic polyanhydride) was introduced into the flask and stirred vigorously. The polyanhydride was taken in such quantity that the free acid formed in its decomposition was completely soluble in the water at the given temperature. At definite intervals 20 ml samples were taken from the solution and filtered; the carboxylic groups in 15 ml of the filtrate were determined by titration with caustic potash solution using phenolphthalein (Table 2).

The solutions remaining after the experiment were boiled for 1 hour and evaporated until crystallization commenced, the precipitate filtered off and dried, and its acid titer and melting point determined. The values found corresponded closely to the acid titers and melting points of free adipic and sebacic acids.

Hydrolysis in alkaline medium. 0.2084 g sebacic polyanhydride was added to 200 ml 0.02 N caustic potash, warmed to the required temperature. The amount of alkali taken was such that about 1 mole of it remained after neutralization of all the sebacic acid formed. The mixture was stirred vigorously and samples were taken. The

acid titer was obtained by titrating the excess alkali with 0.02 N sulphuric acid. A control experiment was carried out simultaneously (Table 3).

Using the constants found and the equation $A = \frac{2.303 \cdot R \cdot T_2 \cdot T_1 \log \frac{kT_2}{kT_1}}{T_2 - T_1}$, the hydrolysis activation energy was calculated and found to equal 9070 cal. Temperature coefficient 1.63.

SUMMARY

1. The quantitative characteristics of the hydrolysis of α-polyanhydrides of adipic and sebacic acids in aqueous and alkaline media are given. The accelerating influence of rise in temperature and of the presence of hydroxyl ions on the hydrolysis has been shown. The rate constants, temperature coefficient and activation energy of sebacic polyanhydride hydrolysis in alkaline medium have been determined.

2. A difference in ease of hydrolysis of adipic and sebacic polyanhydrides has been shown.

LITERATURE CITED

[1] J. W. Hill, J. Am. Chem. Soc. 52, 4110 (1930).

[2] J. W. Hill and W. H. Carothers, J. Am. Chem. Soc. 54, 1569 (1932).

[3] J. W. Hill, J. Am. Chem. Soc. 54, 4105 (1932).

[4] J. W. Hill and W. H. Carothers, J. Am. Chem. Soc. 55, 5023 (1933).

[5] V. V. Korshak, The Chemistry of High Molecular Weight Compounds (Acad. Sci. USSR Press, 1950). 11.

[6] V. V. Korshak and V. V. Golubev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1946, 185.

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CHANGES IN PHENOLIC ETHERS DURING CATALYTIC HYDROGENATION

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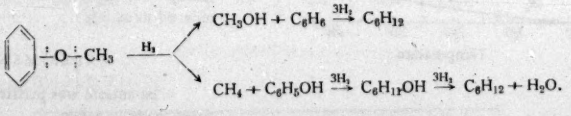
As is known, oxygen compounds of neutral character form one of the component parts of the tar from the semicarbonization of coal, peat and shale. The composition of the "neutral oil" and the catalytic changes in its components have as yet been insufficiently studied. It seemed to us of interest to study the behavior of phenolic ethers, primarily anisole, on catalytic hydrogenation.

Sabatier and Senderens [1] have established that phenolic ethers are converted to the corresponding cyclohexanol ethers by finely divided nickel at 150° in an atmosphere of hydrogen. At the same time hydrogenolysis of the side chain was observed, with the formation of benzene, phenol, cyclohexanol and cyclohexane. At temperatures above 300° hydrogenolysis of the side chains of the original ether molecules proceeds exclusively. Rupture of phenolic ethers in similar conditions has also been observed by a number of other workers[2-5]; it has been shown that increased pressure of hydrogen favors the formation of hydrogenated ethers [6-7].

The purpose of the present work was to examine the influence of the temperature and pressure of hydrogen on the nature of the changes in anisole in contact with a nickel-alumina catalyst containing 10 and 20% of finely divided nickel. The catalyst was prepared by the method of N. D. Zelinsky and V. I. Komarevsky [8], as improved by I. I. Shuikin and coworkers [9].

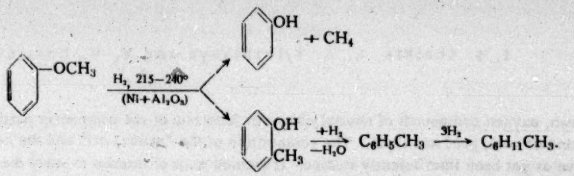
The changes in anisole at atmospheric pressure were studied at 165, 185, 215 and 240°; at the increased hydrogen pressures of 50 and 135 atm. the tests were carried out at 160 and 210°.

No hexahydroanisole was obtained in the hydrogenation experiments at atmospheric pressure; under these conditions the anisole suffered hydrogenolysis of the phenyl-oxygen bond and also evidently of the oxygen-alkyl bond, with subsequent hydrogenation of the hydrogenolysis products:



The products of the catalysis experiments carried out at 165 and 185° consisted of benzene, cyclohexane, methyl alcohol, unchanged anisole, water and a slight oily residue, which was not studied further. The gaseous reaction products were diluted with excess hydrogen and contained a considerable amount of carbon monoxide (8.3% at 185° and 2.8% at 240°); the methane content was 0.5 - 0.7% at 185° and 4.4% at 240°. The presence of carbon monoxide is evidently explained by decomposition of the methyl alcohol, which was confirmed by a specially arranged experiment with pure methyl alcohol at 180°. It may therefore be assumed that the phenol formed under these conditions is completely hydrogenated to cyclohexanol, which in turn is further reduced to cyclohexane. With increase in temperature to 215 and 240°, the reaction involving rupture of the bond between the oxygen and the methyl group predominates, which results in an increase in methane content and decrease in carbon monoxide content of the gaseous reaction products (Figure 1). The catalysis reaction products contain phenols (12.5% at 215° and 30% at 240°). In the phenolic part of the products of both experiments, phenol, identified as tribromophenol, and o-cresol, whose presence was proved by converting it to o-cresylglycolic acid (m.p. 151-152°) were found. The

non-phenolic part of the product contained benzene, cyclohexane and a small quantity of unsaturated compounds together with unchanged anisole. Further, in an intermediate fraction 90-115° obtained on distilling the non-phenolic part of the product, toluene was obtained and converted to benzoic acid, of m.p. 121-121.5°, by oxidation with permanganate according to Ullmann's method [10]. On further treatment of this fraction a hydrocarbon with n_D^{20} 1.4240, evidently methylcyclohexane, was obtained as the monohydrate; the small quantity obtained did not allow a more detailed analysis. It may therefore be assumed that the toluene is a reduction product of the o-cresol formed as a result of isomerization of anisole. Thus the changes in anisole at raised temperatures follow for the most part the following scheme:



Experiments carried out with hexahydroanisole at 215° showed that hydrogenolysis took place much more quickly in this case than in the treatment of anisole under otherwise identical conditions. Hexahydroanisole was completely decomposed; the reaction product consisted of cyclohexane (83.5%), benzene (4.4%) and water (11%). The gaseous reaction products together with the excess hydrogen had the following composition: CO_2 0.4, C_nH_{2n} 0.5, CO 0.5, H_2 91.9 and CH_4 6.7%. The results of these experiments show that the hydrogenolysis of hexahydroanisole in the conditions used takes place for the most part at the bond between the oxygen atom and the alkyl group:

$$C_6H_{11}-O-CH_3 \xrightarrow{H_2} CH_4 + C_6H_{11}OH \xrightarrow[-H_2O]{+H_2} C_6H_{12} \longrightarrow C_6H_6 + 3H_2.$$

Thus on comparing the results of hydrogenation experiments with anisole and hexahydroanisole, it appears that in the conditions used by us hydrogenolysis of the anisole methoxy group takes place at a much greater rate than its hydrogenation in hexahydroanisole.

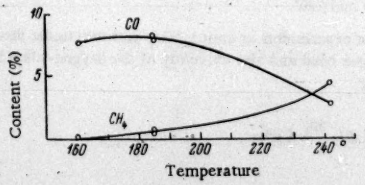


Fig. 1. Relationship between CO and CH_4 content in the gaseous reaction products and the temperature of anisole hydrogenation.

In the hydrogenation of anisole at an initial hydrogen pressure of 50 atm. and 160° hexahydroanisole was obtained in 82.5% yield. On raising the temperature to 210° the degree of hydrogenolysis of the original anisole, and also of the hexahydroanisole formed was raised, while the yield of the latter was reduced to 48.3%.

EXPERIMENTAL

The anisole was purified from phenol and distilled twice in vacuo.

B. p. 70.5° (40 mm), d_4^{20} 0.9960, n_D^{20} 1.5170. Literature data [11]: b.p. 153.75° (760 mm), 73.3° (47 mm), d_4^{20} 0.99402, n_D^{20} 1.5170.

Changes in anisole at atmospheric pressure. The experiments were carried out by the flow method using a nickel-alumina catalyst. The anisole was passed through a catalysis tube with a volume rate of 0.07 - 0.2. Hydrogen was added from an electrolysis apparatus at a rate of 4.7 liters/hour. The molar ratio of hydrogen to anisole was 3.3 - 3.6 : 1. Before carrying out each experiment the catalyst was reduced with hydrogen at 360°. Its activity was checked by reducing benzene at 180°. After the experiments in which the formation of phenols was observed, the catalyst was regenerated by air oxidation for 4 hours at 360° followed by reduction with hydrogen. The catalysis products were washed with water to extract the methyl alcohol. The latter was then distilled from the water and identified by conversion to the 3,5-dinitrobenzoate (melting point of the dinitrobenzoate obtained 107°). No depression was obtained on taking a mixed melting point. The catalyst product was treated with a 10% caustic soda solution

to separate the phenols. After acidification of the alkaline extract, the phenols were extracted with ether, dried with sodium sulfate and distilled under reduced pressure. Phenol was identified as tribromophenol with m.p. 95° (from benzene), the cresols by the reaction with chloroacetic acid [12]. The catalysis products remaining after the removal of the phenolic part were distilled on a reactifying column with an efficiency of 34 theoretical plates. The benzene was determined by sulfonation, the unsaturated material by Kaufmann's method. The results of some typical experiments are given in Tables 1 and 2.

TABLE 1

Composition of the Liquid Reaction Products

Experiment No.	Temperature	Volume rate	Quantity of anisole taken (in g)	Yield of catalysis product (as % of original anisole)	Composition of catalysis product (%)							
					Cyclohexane	Benzene	Methanol	Phenols	Unsaturated compounds	Unchanged anisole	Water	Unidentified residue
1	167°	0.08	12.5	86.0	31.2	1.5	4.0	—	—	49.8	6.5	3.3
2	167	0.07	30.0	89.5	43.7	1.2	3.0	—	—	43.0	5.6	1.5
3	185	0.08	82.0	96.6	40.5		1.3	Traces	—	26.4	24.0	3.8
4	185	0.07	11.5	69.0	45.4	10.1	—	"	—	26.6	9.4	2.3
5	185	0.07	17.3	70.0	37.4	15.0	1.7	"	—	28.2	10.1	1.7
6	185	0.20	42.2	86.0	33.4		1.8	"	—	47.0	6.9	5.5
7	185	0.13	40.6	83.0	34.6		2.4	"	—	51.0	7.1	1.5
8	185	0.14	30.2	75.0	42.2		1.4	"	—	40.0	12.2	1.5
9	215	0.08	25.5	80.0	42.0		—	12.5	0.7	19.2	8.0	5.4
10	242	0.08	37.2	77.0	7.8	13.9	—	30.1	2.0	14.1	7.1	7.0

TABLE 2

Composition of Gaseous Reaction Products

Experiment No.	Temperature of experiment	Composition of the gas (as % of the volume)				
		CO_2	C_nH_{2n}	CO	H_2	CH_4
5	185°	0.5	1.2	8.3	87.6	0.5
1	167	—	0.6	7.4	91.8	0.4
6	185	0.3	0.9	7.9	90.3	0.7
10	242	—	0.6	2.8	92.0	4.4

TABLE 3

Experiment No.	Temperature	Initial pressure (atm.)	Time of hydrogenation (in hrs.)	Composition of catalysis product					
				C_6H_{12}	$C_6H_{11}OCH_3$	$C_6H_{11}OH$	CH_3OH	$C_6H_5OCH_3$	Residue
1	160°	135	5	2.0	77.5	4.5	0.8	—	6.4
2	160	50	5	0.1	82.5	5.8	0.04	—	9.0
3	210	50	10	13.6	48.3	16.4	4.8	6.1	4.3

The benzene-cyclohexane fraction separated from the catalysis product of experiments 4 and 10 was separated chromatographically on "ShSM" silica gel. In experiment 10, cyclohexane with d_4^{20} 0.7790 and n_D^{20} 1.4260, benzene with d_4^{20} 0.8785 and n_D^{20} 1.5002 and unsaturated material with n_D^{20} 1.4445 and bromine number 192, evidently cyclohexene, were obtained.

The method of carrying out the experiments with hexahydroanisole and the analysis of the reaction products was similar to those described above. In the experiments the hexahydroanisole used was obtained by hydrogenation of anisole at raised hydrogen pressure. Gas analysis was carried out in a VTI apparatus.

Changes in anisole under increased hydrogen pressure. The experiments on anisole hydrogenation under increased hydrogen pressure were carried out in a rocking autoclave with electric heater. Hydrogenation was achieved using a nickel-alumina catalyst (20% Ni), in an amount 13% of the weight of the original anisole. 65 g anisole was taken for each experiment. The catalysis product, after centrifugal separation from the catalyst, was dried with ignited potassium carbonate and distilled on a rectifying column with an efficiency of 34 theoretical plates. The experimental results are given in Table 3.

In the distillation at 742 mm of 62.1 g catalysis product from experiment 3 the data given in Table 4 and Figure 2 were obtained.

TABLE 4

Products of the Catalytic Hydrogenation of Anisole at 210° and an Initial Pressure of 50 Atm.

Fraction No.	Boiling range of fraction	Fraction yield			n_D^{20}	d_4^{20}
		in ml	in g	as % weight		
1	53.5— 54.0°	3.9	5.5	8.7	—	—
2	54.0— 79.0	3.0				
3	79.0— 80.5	6.2	5.0	9.8	1.4263	0.7785
4	80.5—115.0	1.2	1.0		1.4265	—
5	115.0—131.2	2.4	2.3	3.7	1.4328	—
6	132.2—132.4	24.0	21.0	42.7	1.4348	0.8790
	132.4—135.0	6.0	5.5		1.4356	—
7	135.0—151.0	2.2	2.0	3.2	1.4842	—
8	151.0—152.0	4.4	4.4	7.1	1.4922	—
9	152.0—158.0	0.9	0.9	15.8	1.4704	
10	158.0—159.0	9.3	8.9		1.4652	0.9530
11	Residue	—	2.3	3.7	—	—

Note: The 1st and 2nd fraction contained methyl alcohol and cyclohexane, the 3rd fraction consisted of cyclohexane, the 6th fraction consisted of hexahydroanisole, the 8th fraction contained cyclohexanol mixed with anisole, the 10th fraction consisted of cyclohexanol.

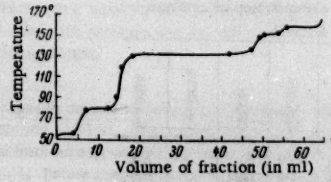


Fig. 2. Distillation curve of the catalysis product from the hydrogenation of anisole at 210° and 50 atm. pressure.

The methyl alcohol present in the combined fractions 53.5 - 79° was washed with water and the aqueous extract analyzed quantitatively by oxidation with chromic acid [13]. The cyclohexane remaining after separation of the methyl alcohol was combined with the 3rd fraction, dried with calcium chloride and distilled over sodium. The hexahydroanisole separated from the 6th fraction had the following properties:

B. p. 132.2 - 132.4° (742 mm), d_4^{20} 0.8790, n_D^{20} 1.4348; MR_D 33.83. $C_6H_{14}O$. Calc. MR_D 33.97.

In the literature the following properties of hexahydroanisole are given [5]: b.p. 135° (760 mm), d_4^{20} 0.8790, n_D^{20} 1.43438.

The cyclohexanol in the 8th fraction was determined by titration with a 0.4 N solution of 3,5-dinitrobenzoyl chloride in dioxane with subsequent back titration of the free acids with 0.01 N caustic soda solution [14]. The 10th fraction appeared to be pure cyclohexanol and on distillation solidified in the condenser as colorless crystals. The cyclohexanol had d_4^{25} 0.9530, n_D^{25} 1.4652; the melting point of the 3,5-dinitrobenzoate was 111.5°. According to the literature data [15]: cyclohexanol has b.p. 160.9° (760 mm), d_4^{22} 0.9471, n_D^{22} 1.4650; melting point 3,5-dinitrobenzoate 112° [16].

SUMMARY

1. The changes in anisole on hydrogenation on nickel-alumina catalyst at 165, 185, 215 and 240° and atmospheric pressure, and also at an initial hydrogen pressure of 50 and 135 atm., have been studied.

2. It has been shown that at atmospheric pressure the anisole, besides undergoing hydrogenolysis of the phenyl-oxygen and oxygen-alkyl bonds, is isomerized to o-cresol; no hexahydroanisole is formed. On hydrogenation of anisole at an initial hydrogen pressure of 50 atm. and 160°, hexahydroanisole is formed in 82.5% yield.

LITERATURE CITED

[1] P. Sabatier, J. B. Senderens, Bull. soc. chim. (3), 33, 616 (1905).

[2] A. Mailhe and M. Murat, Bull. soc. chim. (4), 11, 122 (1912).

[3] W. Funasaka, C. Jokokawa, K. Hayashi, T. Kawamura, H. Fujito and S. Suga, J. Chem. Soc. Japan, Ind. Chem. Sect. 52, 148 (1949); Chem. Abs. 45, 2176d (1951).

[4] Maseo Tomita and Chiaki Tani, J. Pharm. Soc. Japan 64, 242 (1944); Chem. Abs. 45, 5115f (1951).

[5] E. Waser, H. Sonnter, C. Landweer and C. Laza, Helv. Chim. Acta 12, 418 (1929).

[6] V. N. Ipatyev and Lugovoy, J. Russ. Chem. Soc. 46, 470 (1914).

[7] E. M. Van Duzee and H. Adkins, J. Am. Chem. Soc. 57, 147 (1935).

[8] N. D. Zelinsky and V. I. Komarevsky, Ber. 57, 667 (1924).

[9] N. I. Shuikin, Kh. M. Minachev and L. M. Feofanova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, 97.

[10] F. Ullmann, J. Bex Uzbachian, Ber. 36, 1798 (1903).

[11] R. R. Dreisbach and R. A. Martin, Ind. Eng. Chem. 41, 2875 (1949).

[12] T. Akita, Bull. Inst. Phys. Chem. Research (Tokyo) 21, 152 (1942); Chem. Abs. 43, 7867 (1943).

[13] O. Blank and H. Finkenbeimer, Ber. 39, 1326 (1906).

[14] I. V. Berezin, Dissertation (Moscow State Univ. 1953).

[15] N. Zelynsky, Ber. 34, 2800 (1901).

[16] K. Bauer, The Analysis of Organic Compounds (Foreign Lit. Press 1953), 49.

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ORGANIC INSECTOFUNGICIDES

XXI. SYNTHESIS OF MIXED ESTERS OF DITHIOPHOSPHORIC ACID

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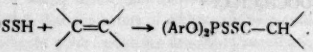
Organic phosphorus compounds are finding constantly greater use in agriculture as active agents for combatting various plant parasites. In particular, the various mixed esters of the thio- and dithiophosphoric acids find extensive use. The dithiophosphoric acid derivatives are characterized by a comparatively low toxicity for warm-blooded animals, and together with this show quite a high insecticidal and acaricidal activity, which creates favorable conditions for their use in agriculture. In connection with the above, the synthesis and study of various dithiophosphoric acid derivatives is of great interest both for the accumulation of material on the dependence of the insecticidal activity of these compounds on their structure, and for a study of the properties and reactions of the given group of compounds.

A new simple method was recently developed [1] for obtaining the mixed esters of dithiophosphoric acid, representing the greatest interest relative to utilization as agents for combatting plant parasites, which consists in the addition of the acid esters of dithiophosphoric acid to the double bond of various unsaturated compounds. This reaction is a simple and convenient way of synthesizing esters of dithiophosphoric acid that contain various substituents in the ester radical. Up to now the reaction of unsaturated compounds has been studied with many dialkyl dithiophosphoric acids and active insecticides have been found among the obtained compounds [2]. The reaction of diaryl dithiophosphoric acids with unsaturated compounds has been left completely unstudied, although this question is of great interest. Also of great interest is a study of the reaction of dialkyl dithiophosphoric acids with unsaturated compounds that contain two substituents on the carbons adjacent to the double bond.

In this communication we describe the results of studying the disclosed reaction in the two indicated directions. The experiments that we ran revealed that the reaction of the acid aromatic esters of dithiophosphoric acid with unsaturated compounds proceeds in a manner completely analogous to that of the corresponding aliphatic compounds, and the full mixed esters of dithiophosphoric acid are obtained in satisfactory yields:



This reaction was studied on the examples of adding diphenyl dithiophosphate and 4,4'-dichlorodiphenyl dithiophosphate to acrylonitrile and the esters of acrylic, methacrylic and maleic acids. In view of the fact that the mixed dithiophosphoric acid esters synthesized by us are liquids, failing to distill in high vacuum, their purification and isolation present certain difficulties. All of the obtained compounds were purified chromatographically, with absorption of the impurities from benzene solution on activated aluminum oxide. The compounds that we synthesized and their properties are presented in Table 1. All of these compounds are very weak insecticides.

At the same time we studied the addition of dialkydithiophosphoric acids to the esters of itaconic, citraconic and chloromaleic acids. The reaction with the esters of chloromaleic acid proceeds at a considerably slower rate than it does with the corresponding esters of maleic acid, and the mixed esters of dithiophosphoric acid are obtained in low yields. Apparently, reaction in these cases proceeds contrary to the Markovnikov rule,

TABLE 1

Aromatic Mixed Esters of Dithiophosphoric Acid

Formula	Yield (in %)	d_4^{20}	n_D^{20}	Analysis for P (in %) found	Analysis for P (in %) calculated
$(C_6H_5O)_2PSSCH_2CH_2CN$	45	1.2448	1.6030	9.10, 9.12	9.25
$(C_6H_5O)_2PSSCH_2CH(CH_3)COOCH_3$	73	1.2227	1.5792	8.09, 8.04	8.12
$(C_6H_5O)_2PSSCH_2CH_2COOCH_3$	47	1.2577	1.5862	8.46, 8.30	8.43
$(C_6H_5O)_2PSSCHCOOC_2H_5$ $CH_2COOC_2H_5$	54	1.2783	1.5468	6.57, 6.72	6.83
$(ClC_6H_4O)_2PSSCH_2CH_2CN$	55	1.3755	1.6078	8.00	7.67
$(ClC_6H_4O)_2PSSCH_2CHCOOCH_3$ CH_3	74	1.3182	1.5871	7.15, 7.13	6.87
$(ClC_6H_4O)_2PSSCH_2CH_2COOCH_3$	45	1.3379	1.5911	7.20, 7.28	7.11
$(ClC_6H_4O)_2PSSCHCOOC_2H_5$ $CH_2COOC_2H_5$	44	1.2545	1.5371	6.26, 5.93	5.94

TABLE 2

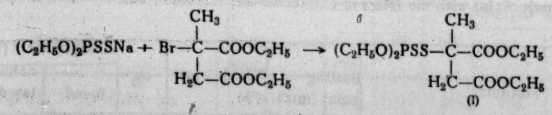
Chlorine-Containing Mixed Esters of Dithiophosphoric Acid

Formula	Boiling point (mm)	Yield (%)	d_4^{20}	n_D^{20}	Analysis for P (%) found	Analysis for P (%) calculated
$(CH_3O)_2PSSCHCOOC_2H_5$ $ClCHCOOC_2H_5$	136° (0.18)	28	1.2902	1.5110	8.75 8.18	8.49
$(C_2H_5O)_2PSSCHCOOC_2H_5$ $ClCHCOOC_2H_5$	125—128 (0.15)	30	1.2151	1.5010	7.71, 7.50	7.86
$(C_2H_5O)_2PSSCHCOOCH_3$ $ClCHCOOCH_3$	137—140 (0.2)	31	1.2879	1.5103	8.17, 8.44	8.49
$(C_2H_5O)_2PSSCHCOOCH_2CH_2Cl$ $CH_2COOCH_2CH_2Cl$	135 (0.15)	15	1.2660	1.5074	7.76	7.25

which is supported to a certain degree by the properties of the obtained compounds, in particular, their relative high stability to hydrolysis, whereas the compounds with both a halogen and sulfide group on the same carbon atom are hydrolyzed with relative ease to yield carbonyl compounds and hydrogen halides. Although it should be mentioned that in our cases it is also possible for reaction to proceed by the Markovnikov rule, still it is difficult to isolate the reaction products due to their decomposition into the starting components during distillation. The compounds obtained by us and their properties are presented in Table 2. The reaction of the dialkyl dithiophosphoric acids with the esters of citraconic acid also proceeds very slowly, and the corresponding dithiophosphoric acid esters are formed in relatively low yields:

$$(RO)_2PSSH + \begin{matrix} CH_3-C-COOR' \\ \| \\ HC-COOR' \end{matrix} \rightarrow \begin{matrix} CH_3-CH-COOR' \\ | \\ (RO)_2PSSCH-COOR'. \end{matrix}$$

In this case also the addition goes contrary to the Markovnikov rule. To prove the validity of such a position we synthesized O,O-diethyl-S-1,2-dicarbethoxyethyl dithiophosphate (I) through the known [3] (4,5)-α-methyl-α-bromosuccinic acid:



which in its properties proved to be different from the ester obtained by the addition of diethyl dithiophosphoric acid to the ethyl ester of citraconic acid, which is direct proof for the structure of this ester.

The reaction of the ethyl ester of itaconic acid with diethyl dithiophosphoric acid proceeds in a similar manner. The compounds obtained by us and their properties are presented in Table 3. Some of the compounds given in this table show fairly high insecticidal activity, but they are inferior in this respect to the earlier described compounds [2].

EXPERIMENTAL

1. Reaction of diaryl dithiophosphoric acids with unsaturated compounds. The starting diaryl dithiophosphoric acids were obtained by reacting phenols with phosphorus pentasulfide under heating [2]. Equimolar amounts of the diaryl dithiophosphoric acid and unsaturated compound were heated for several hours on the water bath at 80-90° (in the case of 4,4'-dichlorodiphenyl dithiophosphate the reaction also proceeds at room temperature). On conclusion of reaction the obtained oil was washed several times with 10% aqueous soda solution, then with water, and dried over anhydrous calcium chloride. Then the unsaturated compound was distilled from it in vacuo, the residue was dissolved in pure dry benzene, and the benzene solution was passed through a chromatographic column containing activated aluminum oxide. After removal of the impurities, which were adsorbed on the aluminum oxide, the benzene was removed from the solution by vacuum distillation. In this way we obtained analytically pure compounds. The compounds that we obtained and their properties are given in Table 1.

2. Reaction of dialkyl dithiophosphoric acids with the esters of chloromaleic acid. The chloromaleic anhydride used to obtain the chloromaleic acid esters was prepared by the chlorination of maleic anhydride in the presence of anhydrous ferric chloride at elevated temperature. The anhydrides of bromomaleic and dichloromaleic acids were prepared in a similar manner, from which the esters of the corresponding alcohols were prepared in the usual manner. The reaction of the dialkyl dithiophosphoric acids with the esters of the halomaleic acids was run at room temperature, and also with heating for a long time. On conclusion of reaction the obtained oil was washed with soda solution, water, dried, and fractionated in high vacuum. As a result of the experiments made, it was possible to establish that the esters of dichloromaleic acid and of bromomaleic acid fail to react with the dialkyl dithiophosphoric acids under the described reactions. The properties of the compounds that we obtained from the esters of chloromaleic acid are presented in Table 2. To elucidate the influence of a halide in the ester radical we studied the reaction of diethyl dithiophosphate with the 2-chloroethyl ester of maleic acid. In this case the reaction proceeds just as slowly as it does with the esters of the halomaleic acids. The properties of the obtained dithiophosphoric acid mixed ester are presented in Table 2.

3. Reaction of dialkyl dithiophosphoric acids with the esters of citraconic acid. The reaction was run under the earlier described conditions [1], but its duration was many times greater. In some cases, to obtain an appreciable yield of the dithiophosphoric acid mixed ester, it was necessary to run the reaction for several weeks. The reaction mixture was worked up as described above in Section 2. The compounds obtained by us and their properties are presented in Table 3. All of the synthesized compounds are new.

4. Preparation of O,O-diethyl S-1-methyl-1,2-dicarbethoxyethyl dithiophosphate (I). The starting α-methyl-α-bromosuccinic acid was obtained by the method of [3]. The ethyl ester was prepared from this acid in the usual manner, which was then used for subsequent syntheses. The dithiophosphoric acid mixed ester was

TABLE 3

Properties of Mixed Esters of Dithiophosphoric Acids, Obtained by the Reaction of Dialkyl Dithiophosphoric Acids with the Esters of Citraconic and Itaconic Acids

Formula	Boiling point (mm)	Yield (%)	d_4^{20}	n_D^{20}	Analysis for P (%) found	Analysis for P (%) calculated
$(CH_3O)_2PSSCHCOOCH_3$ $CH_3CHCOOCH_3$	137° (0.22)	25	1.2737	1.5240	9.27, 9.30	9.79
$(C_2H_5O)_2PSSCHCOOCH_3$ $CH_3CHCOOCH_3$	117—119 (0.07)	12	1.2004	1.5042	8.44, 8.38	9.00
$(C_4H_9O)_2PSSCHCOOCH_3$ $CH_3CHCOOCH_3$	120—122 (0.1)	14	1.0910	1.4950	7.80, 7.85	7.75
$(iso\text{-}C_4H_9O)_2PSSCHCOOCH_3$ $CH_3CHCOOCH_3$	141 (0.1)	13	1.1301	1.4880	7.50, 7.90	7.75
$(CH_3O)_2PSSCHCOOC_2H_5$ $CH_3CHCOOC_2H_5$	120—122 (0.12)	25	1.2038	1.4950	8.90, 9.08	9.00
$(C_2H_5O)_2PSSCHCOOC_2H_5$ $CH_3CHCOOC_2H_5$	135—137 (0.25)	17	1.1445	1.4904	8.22, 8.27	8.32
$(C_3H_7O)_2PSSCHCOOC_2H_5$ $CH_3CHCOOC_2H_5$	140 (0.2)	14	1.0900	1.4902	7.45, 7.60	7.75
$(C_4H_9O)_2PSSCHCOOC_2H_5$ $CH_3CHCOOC_2H_5$	143 (0.08)	11	1.0806	1.4895	7.42, 7.46	7.23
$(iso\text{-}C_4H_9O)_2PSSCHCOOC_2H_5$ $CH_3CHCOOC_2H_5$	150—152 (0.22)	22	1.0789	1.4855	8.05	7.23
$(CH_3O)_2PSSCHCOOC_3H_7$ $CH_3CHCOOC_3H_7$	135 (0.45)	10	1.1677	1.4925	7.68	8.32
$(C_2H_5O)_2PSSCHCOOC_3H_7$ $CH_3CHCOOC_3H_7$	145 (0.1)	18	1.1283	1.4908	7.50, 7.60	7.75
$(iso\text{-}C_3H_7O)_2PSSCHCOOC_3H_7$ $CH_3CHCOOC_3H_7$	155 (0.3)	15	1.0678	1.4810	6.68	7.23
$(CH_3O)_2PSSCHCOOC_3H_7\text{-}iso$ $CH_3CHCOOC_3H_7\text{-}iso$	125—127 (0.12)	15	1.1557	1.4964	7.73, 7.97	8.32
$(C_2H_5O)_2PSSCHCOOC_3H_7\text{-}iso$ $CH_3CHCOOC_3H_7\text{-}iso$	135 (0.18)	11	1.1369	1.4900	7.32, 7.35	7.75
$(C_2H_5O)_2PSSCHCOOC_4H_9$ $CH_3CHCOOC_4H_9$	154—157 (0.2)	22	1.1041	1.4880	6.94, 6.95	7.23
$(iso\text{-}C_3H_7O)_2PSSCHCOOC_4H_9$ $CH_3CHCOOC_4H_9$	143—145 (0.11)	23	1.1270	1.4851	7.12, 6.91	6.80
$(CH_3O)_2PSSCHCOOC_4H_9\text{-}iso$ $CH_3CHCOOC_4H_9\text{-}iso$	152—153 (0.35)	22	1.1381	1.4870	8.06, 7.45	7.75

TABLE 3 (continued)

Formula	Boiling point (mm)	Yield (%)	d_4^{20}	n_D^{20}	Analysis for P (%) found	Analysis for P (%) calculated
$(C_5H_9O)_2PSSCHCOOC_4H_9$-iso $CH_3CHCOOC_4H_9$-iso	158—162 (0.65)	26	1.1175	1.4852	7.44	7.23
$(C_3H_7O)_2PSSCHCOOC_3H_7$ $CH_3CHCOOC_3H_7$	148 (0.1)	23	1.1157	1.4900	6.72, 6.86	7.23
$(C_4H_9O)_2PSSCHCOOC_3H_7$ $CH_3CHCOOC_3H_7$	160—162 (0.45)	11	1.0789	1.4870	7.00	6.80
$(C_3H_7O)_2PSSCHCOOC_4H_9$ $CH_3CHCOOC_4H_9$	160 (0.2)	22	1.0881	1.4878	7.20, 6.86	6.80
$(C_4H_9O)_2PSSCHCOOC_4H_9$ $CH_3CHCOOC_4H_9$	168—170 (0.55)	11	1.0721	1.4876	6.93, 6.68	6.48
$(C_3H_7O)_2PSSCHCOOC_4H_9$-iso $CH_3CHCOOC_4H_9$-iso	135 (1.0)	13	1.0804	1.4871	6.71, 6.55	6.80
$(C_4H_9O)_2PSSCHCOOC_4H_9$-iso $CH_3CHCOOC_4H_9$-iso	158—160 (0.1)	25	1.0706	1.4868	6.20, 6.74	6.48
(iso-C_3H_7O)PSSCH$_2$CHCOOC$_2$H$_5$ $CH_2COOC_2H_5$	168—169 (0.3)	17	1.0636	1.4838	7.81	7.75
$(C_3H_5O)_2PSSCH_2CHCOOC_2H_5$ $CH_2COOC_2H_5$	143—145 (0.17)	38	1.1727	1.4932	8.41, 8.45	8.32

obtained by reacting sodium diethyl dithiophosphate with the ethyl ester of the methylbromosuccinic acid in acetone solution. Into a flask fitted with reflux condenser and mechanical stirrer were charged equimolar quantities of sodium diethyl dithiophosphate and the ethyl ester of the methylbromosuccinic acid in acetone, and the obtained solution was boiled on the water bath until the sodium bromide ceased to precipitate (about 20 hours). After conclusion of reaction the cooled reaction mixture was filtered to remove sodium bromide, the solvent was vacuum-distilled, and the residue, after washing with water and drying, was distilled in high vacuum. The yield was about 20%. B. p. 127° at 0.07 mm, d_4^{20} 1.1911, n_D^{20} 1.5113.

The low yield of the O,O-diethyl S-1-methyl-1,2-dicarbethoxyethyl dithiophosphate is apparently explained by the presence of a side reaction – the cleavage of hydrogen bromide.

This and the other dithiophosphoric acid esters were analyzed for phosphorus by the photocolorimetric method [4] that was recently developed in our laboratory.

Found %: P 8.43, 8.42. $C_{13}H_{25}O_6S_2P$. Calculated %: P 8.33.

5. Reaction of ethyl itaconate with diethyl dithiophosphate. Equimolar amounts of ethyl itaconate and diethyl dithiophosphate in a flask under reflux were heated on the water bath for 20 hours. On conclusion of heating the reaction mixture was washed with soda, water, dried, and distilled in high vacuum. B. p. 143-145° at 0.17 mm, d_4^{20} 1.727, n_D^{20} 1.4932. Yield about 40%.

Found %: P 8.41, 8.45. $C_{13}H_{25}O_6S_2P$. Calculated %: P 8.33.

If the addition had gone in accord with the Markovnikov rule, then the above-described O,O-diethyl S-1-methyl-1,2-dicarbethoxyethyl dithiophosphate should have been formed. However, the compound that we

obtained differs from it in all of its constants, which indicates a different course for the reaction, i. e. in the given case the addition at the double bond is contrary to the Markovnikov rule.

SUMMARY

The addition of dialkyl and diaryl dithiophosphoric acids to the double bond of various unsaturated compounds was studied. It was shown that the diaryl dithiophosphoric acids, the same as the dialkyl dithiophosphoric acids, easily add to unsaturated compounds, forming the full mixed esters of the dithiophosphoric acid. It was established that the addition of the dialkyl dithiophosphoric acids to the esters of chloromaleic, citraconic and itaconic acids proceeds contrary to the Markovnikov rule.

More than forty new compounds were synthesized, some of which appear to be fairly strong insecticides, but all of them are inferior to Carbophos (O,O-diethyl S-1,2-dicarbethoxyethyl dithiophosphate).

LITERATURE CITED

[1] N. N. Melnikov and K. D. Shvetsova-Shilovskaya, Proc. Acad. Sci. USSR 86, 543 (1952); J. Gen. Chem. 23, 1352 (1953) (T. p. 1417). *

[2] K. A. Gar, N. N. Melnikov, Yu. N. Fadeev and K. D. Shvetsova-Shilovskaya, Proc. Acad. Sci. USSR 94, 241 (1954).

[3] W. Autenrieth and C. Pretzell, Ber. 36, 1271 (1903); A. Michael and H. S. Mason, J. Org. Chem. 9, 395 (1944).

[4] N. N. Melnikov, M. L. Galashina, P. B. Nutovich and K. D. Shvetsova-Shilovskaya, Trans. Sci. Research Inst. Fertilizers and Insecticides (State Chem. Press, Moscow, 1955), 154, 89.

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ORGANIC INSECTOFUNGICIDES

XXII. THE REACTION OF DIALKYL CHLOROTHIOPHOSPHATES WITH p-NITROPHENOLS IN THE PRESENCE OF PYRIDINE HYDROCHLORIDE

Z. M. Bakanova, Ya. A. Mandelbaum and N. N. Melnikov

As is known, the main method of obtaining the mixed aliphatic-aromatic esters of thiophosphoric acid is to react dialkyl chlorothiophosphates with the phenolates of the alkali metals or with phenols in the presence of a base [1]. In the absence of bases or carbonates of the alkali metals there is practically no reaction between the dialkyl chlorothiophosphates and phenols, and the corresponding mixed esters cannot be obtained by this procedure. In connection with a study of the thermal decomposition of O,O-diethyl O-4-nitrophenyl thiophosphate and some esters of chloro- and dichlorothiophosphoric acids we undertook a study of the reaction of dialkyl chlorothiophosphates with p-nitrophenol at elevated temperature in the presence of catalytic amounts of various neutral and acidic compounds. The most interesting results were obtained when we ran the indicated reaction in the presence of pyridine hydrochloride. The reaction of the dialkyl chlorothiophosphates with p-nitrophenol was run at 130-145°, and 0.6-0.7 g of pyridine salt was taken per 0.1 mole of ester. The main reaction products in the given case are the S-alkyl O,O-4,4'-dinitrodiphenyl thiophosphates, which are formed in about 25% yield; the other products obtained are hydrogen chloride, ethylene, and the acid esters of phosphoric and thiophosphoric acids.

Apparently, there are a number of consecutive and parallel reactions that take place in the investigated cases, some of which can be depicted by the following schemes:

$$(RO)_2PSCl + HOC_6H_4NO_2 \longrightarrow (RO)_2PSOC_6H_4NO_2 + HCl.$$

$$2\,(RO)_2PSOC_6H_4NO_2 \longrightarrow 2 \begin{matrix} RS \\ RO \end{matrix} \!\!>\!\! P(=O)\!-\!OC_6H_4NO_2 \longrightarrow RSPO(OC_6H_4NO_2)_2 + (RO)_2(RS)PO$$

$(RO)_2(RS)PO \longrightarrow C_2H_4 +$ acid esters of phosphoric and thiophosphoric acids.

This type of reaction was recently observed in our laboratory when we studied the thermal decomposition and isomerization of some esters of chlorothiophosphoric and thiophosphoric acids [2], and also by V. Tichy [3] when he studied the thermal decomposition of O,O-diethyl O-4-nitrophenyl thiophosphate.

EXPERIMENTAL

Reaction of dimethyl chlorothiophosphate with p-nitrophenol. In a flask fitted with reflux condenser, mechanical stirrer and thermometer was placed 16 g of dimethyl chlorothiophosphate, 13.9 g of p-nitrophenol and 0.6 g of pyridine hydrochloride, and the reaction mixture was heated in an oil bath at 125-130° (temperature of the reaction mixture) until hydrogen chloride ceased to evolve (3 hours). The reaction mixture after cooling is a dark viscous oil, partially soluble in water, and showing acid reaction. Treatment of the reaction mixture with a small amount of methyl alcohol gave crystals, which were filtered, and then purified by recrystallization from methyl alcohol. M. p. 108°. The product is completely devoid of thiono sulfur, and by analysis

corresponds to S-methyl O,O-4,4'-dinitrodiphenyl thiophosphate, which from the literature [3] has m. p. 109°. The yield was about 7.5 g or about 50%, based on dimethyl chlorothiophosphate.

Found %: P 8.71, 8.69. $C_{13}H_{11}O_7N_2SP$. Calculated %: P 8.39.

The methyl alcohol was vacuum distilled from the filtrate and the acid esters of the phosphoric acids were removed by washing with water, while unreacted p-nitrophenol was removed from the residue by treatment with 5% soda solution, the acidification of which gave about 5.5 g of p-nitrophenol.

Reaction of diethyl chlorothiophosphate with p-nitrophenol. A mixture of 19 g of diethyl chlorothiophosphate, 13.8 g of p-nitrophenol and 0.7 g of anhydrous pyridine hydrochloride was heated under the above described conditions for 3 hours at 130-140°. Besides hydrogen chloride, the gaseous reaction products were found to contain ethylene and ethyl chloride. On conclusion of heating the reaction product was worked up the same as described above, but ethyl alcohol was used instead of methyl alcohol. Recrystallization from ethyl alcohol gave about 8.5 g of S-ethyl O,O-4,4'-dinitrodiphenyl thiophosphate with m. p. 111° (from the literature, m. p. 112° [3]).

Found %: P 8.4, 8.35; S 7.96, 8.10; N 7.6, 7.58. $C_{14}H_{13}O_7N_2SP$. Calculated %: P 8.07; S 8.34; N 7.3.

Suitable treatment of the ethyl alcohol solution gave about 4 g of unreacted p-nitrophenol.

SUMMARY

The reaction of some dialkyl chlorothiophosphates with p-nitrophenol was studied in the presence of catalytic amounts of pyridine hydrochloride. It was shown that the main products of this reaction are S-alkyl O,O-4,4'-dinitrodiphenyl thiophosphates, which are obtained as the result of disproportionation and cross-esterification reactions.

LITERATURE CITED

[1] G. Schrader, Progr. Chem. 22, 533 (1953); N. N. Melnikov, Progr. Chem. 22, 253 (1953); J. H. Fletcher and J. C. Hamilton, J. Am. Chem. Soc. 70, 3943 (1948); U. S. Patent No. 2471464 (1949).

[2] N. N. Melnikov and D. N. Khokhlov, J. Gen. Chem. 23, 1357 (1953) (T. p. 1421);* S. M. Bakanova, V. I. Lomakina, Ya. A. Mandelbaum and N. N. Melnikov, Trans. Sci. Research Inst. Fertilizers and Insecticides (State Chem. Press, Moscow, 1955), 154, 84.

[3] V. Tichy, Chem. Zvesti 9, 3 (1954).

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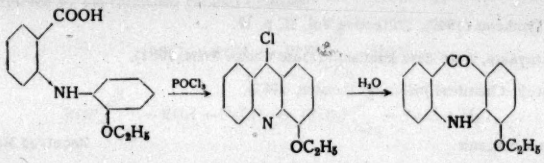
PREPARATION OF THE FLUORESCENT INDICATOR 4-ETHOXYACRIDONE

G. N. Kosheleva

4-Ethoxyacridone is a widely used fluorescent indicator (the fluorescence of its solutions changes from a green to a blue color in ultraviolet light at pH 1.2-3.0). However, the problem of its synthesis has received little attention. The acridone itself, as well as its derivatives, are usually formed by the intramolecular condensation of the corresponding diphenylaminecarboxylic acids in the presence of condensing agents [1, 2], for example, sulfuric acid [3, 5], thionyl chloride, phosphorus pentachloride [4] and phosphorus oxychloride. In the last case the reaction proceeds through an intermediate product – the mesochloro derivative of the acridine [6]. The yield in the presence of sulfuric acid reaches 90% (2-methoxyacridone) [7] and even 96% (acridone) [8]. According to the data of the author [3], in the presence of sulfuric acid the yield of 4-ethoxyacridone is a total of only 48%, since in this case a part of the formed 4-ethoxyacridone is quite rapidly saponified with the formation of 4-hydroxyacridone. The preparation of 4-ethoxyacridone in the presence of other condensing agents has not been described up to now.

We synthesized it from 2-carboxy-2'-ethoxydiphenylamine with the aid of phosphorus oxychloride by the scheme:



We obtained the previously unknown 4-ethoxy-9-chloroacridine, and from it the 4-ethoxyacridone in 79% yield. 4-Ethoxy-9-chloroacridine is a nearly white colorless substance with m. p. 124-125°. It is difficultly soluble in water, and readily soluble in alcohol and dilute acids. Its solutions in acids show an intense green fluorescence in ultraviolet light. It is strongly irritating to the human skin, and especially the mucous membranes. 4-Ethoxyacridone is a yellow crystalline product. In ultraviolet light its solutions change from a green to a blue fluorescence at pH 1.2-3.0, which is in accord with the literature [9, 10].

EXPERIMENTAL

Preparation of 4-Ethoxy-9-Chloroacridine. In a round-bottomed flask fitted with reflux condenser was placed 50 g of 2-carboxy-2'-ethoxydiphenylamine (m. p. 158-160°, with a purity of 98%) and 200 ml of phosphorus oxychloride, the mixture dissolved by heating, and then boiled for 1 hour. Then the reflux condenser was replaced by a descending condenser, and 120 ml of phosphorus oxychloride was distilled off. The residue was poured into 1 liter of water, the solution filtered from a small amount of tarry impurities, and the filtrate treated with 10% sodium hydroxide solution until faintly alkaline to brilliant yellow paper. The obtained 4-ethoxy-9-chloroacridine was filtered, washed with water, and dried. The yield was 43.5 g (89%). M. p. 124-125°.

Found %: Cl 13.85, 13.82. $C_{15}H_{12}ONCl$. Calculated %: Cl 13.7.

Preparation of 4-ethoxyacridone. 4-Ethoxy-9-chloroacridine (43.8 g) was dissolved in 750 ml of water and 23 ml of concentrated hydrochloric acid. The solution was heated with stirring for 1.5 hours. The resulting 4-ethoxyacridone precipitate was filtered, washed with 100 ml of water, and dried at 60-70°. Yield of 4-ethoxyacridone 36.5 g (79%). The substance was recrystallized from 70 ml of an aniline-glacial acetic acid mixture (1:2.5 by volume) with the addition of activated charcoal. The recrystallization yield was 90% of the taken amount.

Found %: N 5.96, 6.16. $C_{15}H_{13}O_2N$. Calculated %: N 5.86.

SUMMARY

4-Ethoxyacridone was synthesized in 79% yield by the intramolecular condensation of 2-carboxy-2'-ethoxydiphenylamine in the presence of phosphorus oxychloride. The previously unknown intermediate product of this reaction, namely 4-ethoxy-9-chloroacridine, was isolated in the pure state.

LITERATURE CITED

[1] Merck Index: An Encyclopedia for Chemistry (Merck Co., U. S. A., 1952), 1063.

[2] N. N. Vorozhtsov, Fundamentals of the Synthesis of Intermediate Products and Dyes (State Chemical Press, 1950), p. 760.

[3] K. Matsumura, J. Am. Chem. Soc. 49, 810 (1927).

[4] G. Schroeter and O. Eisleb, Ann. 367, 144 (1909).

[5] L. Villemey, Ann. chim. (12) 5, 570 (1950).

[6] O. Magidson and A. Grigorowski, Ber. 66, 866 (1933).

[7] F. Ullmann and H. Kipper, Ber. 38, 2125 (1905).

[8] Organic Syntheses (1949), Collective Vol. II, p. 19.

[9] Yu. V. Karyakin, Acid-Base Indicators (State Chem. Press, 1951).

[10] O. Tomicek, Chemical Indicators (London, 1951).

Institute of Chemical Reagents

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ORGANIC INSECTOFUNGICIDES

XXIII. PREPARATION OF DIALKYL CHLOROTHIOPHOSPHATES

N. N. Melnikov, Ya. A. Mandelbaum, V. I. Lomakina and Z. M. Bakanova

The mixed esters of thiophosphoric acid find steadily increasing use as contact and systemic insecticides, and the number of such compounds is constantly growing. One of the most extensively used methods to obtain these compounds is the reaction of dialkyl chlorothiophosphates with either the phenolates or alcoholates of the alkali metals. The dialkyl chlorothiophosphates needed for the synthesis of the thiophosphoric acid mixed esters are usually obtained by the reaction of phosphorus thiotrichloride with the alkali alcoholates of the corresponding alcohols at low temperature [1-4]. However, the use of alkali metal alcoholates to synthesize the dialkyl chlorothiophosphates in any large amount is associated with considerable inconvenience, for which reason as early as 1949 a method was proposed for the preparation of diethyl chlorothiophosphate and its homologs from phosphorus thiotrichloride, the alcohol and sodium hydroxide [5]. In 1954 a British patent [6] was published on a similar method of preparing the dimethyl and diethyl chlorothiophosphates.

The preparation of dialkyl chlorothiophosphates from phosphorus thiotrichloride, the alcohol and sodium hydroxide can be depicted by the following general schemes:

$$PSCl_3 + ROH \longrightarrow ROP(=S)Cl_2 + HCl,$$

$$ROP(=S)Cl_2 + ROH + NaOH \longrightarrow (RO)_2P(=S)Cl + NaCl + H_2O.$$

Here the formation of the full esters of thiophosphoric acid can occur as the result of side reactions.

$$(RO)_2P(=S)Cl + ROH + NaOH \longrightarrow (RO)_3PS + NaCl + H_2O$$

and also the hydrolysis of the phosphorus thiotrichloride, alkyl dichlorothiophosphate and dialkyl chlorothiophosphate in the presence of excess alkali, leading to the formation of the salts of the thiophosphoric acids.

In connection with the above the rates of the main and side reactions should be taken into consideration in selecting the conditions to be used for preparing the individual chlorothiophosphoric acid esters.

In the present study we developed conditions for obtaining not only the dialkyl chlorothiophosphates with the same hydrocarbon radicals, but also the mixed esters of chlorothiophosphoric acid.

EXPERIMENTAL

Preparation of dimethyl chlorothiophosphate. In a flask fitted with reflux condenser, thermometer, dropping funnel and mechanical stirrer, the last making not less than 200 revolutions a minute, was placed 204 g

of phosphorus thiotrichloride, the latter cooled in a cooling mixture to −10° to −12°, and 120 g of methyl alcohol was added with stirring. (The temperature should not exceed 0° during the methyl alcohol addition.) After this the reaction mass was cooled to −10° and at this temperature was gradually added 122-125 g of sodium hydroxide in 180 ml of water. (The temperature of the reaction mixture should not exceed 0° during the sodium hydroxide addition.) After all of the sodium hydroxide had been added the reaction mixture was stirred for 2 hours (here the temperature should not exceed 20°), after which 300-350 ml of water was added to the reaction mixture and stirring continued for 15 minutes. After standing the oil layer was separated, dried over calcium chloride, and vacuum-distilled. The yield of pure dimethyl chlorothiophosphate was 150-169 g (85-87%).

B. p. 66-67° (16 mm), d_0^0 1.3350, n_D^{25} 1.4840.

Powdered sodium hydroxide can also be used to obtain the dimethyl chlorothiophosphate, it being slowly added to the reaction mixture instead of the aqueous solution. In this case the yield of dimethyl chlorothiophosphate was 3-4% higher.

Preparation of O-methyl O-ethyl chlorothiophosphate. As starting products for the synthesis of the mixed dialkyl chlorothiophosphates we used the alkyl dichlorothiophosphates, which were obtained by heating equimolar amounts of the anhydrous alcohol and phosphorus thiotrichloride [2]. To prepare the mixed dialkyl chlorothiophosphates it is better to start from an alcohol with lower molecular weight than the alcohol taken to prepare the alkyl dichlorothiophosphate.

To 53.7 g of ethyl dichlorothiophosphate, cooled to −10°, was added 45 ml of methyl alcohol, and then 13.5 g of powdered sodium hydroxide was added in 45 minutes with good stirring and cooling. After the indicated amount of sodium hydroxide had been added the reaction mixture was stirred at 20° for 2 hours, and then 100 ml of water was added to the reaction mass. After all of the precipitate had dissolved the mixture was allowed to stand, the oil layer separated, dried over anhydrous calcium chloride, and fractionally distilled in vacuo. Yield 48 g (91%).

B. p. 73-74° (18 mm), d_4^{20} 1.2739, n_D^{25} 1.4734.
Found %: P 17.85; Cl 20.36. $C_3H_8O_2ClP$. Calculated %: P 17.7; Cl 19.96.

Aqueous sodium hydroxide solution can also be used to prepare the methyl ethyl chlorothiophosphate. In this case the above indicated amount of sodium hydroxide was dissolved in 20 ml of water. The yield when aqueous sodium hydroxide solution was used was 87-90%.

Preparation of O-methyl O-isopropyl chlorothiophosphate. From 17.5 g of isopropyl dichlorothiophosphate, 8 ml of methyl alcohol and 4.3 g of sodium hydroxide under the above described conditions we obtained after suitable treatment 12.5 g (75.7%) of O-methyl O-isopropyl chlorothiophosphate.

B. p. 87-88° (22 mm), d_4^{20} 1.1879, n_D^{20} 1.4680.
Found %: P 16.3, 16.7; Cl 18.9. $C_4H_{10}O_2ClP$. Calculated %: P 16.4; Cl 18.8.

Preparation of O-methyl O-butyl chlorothiophosphate. From 20.7 g of butyl dichlorothiophosphate, 8 ml of methyl alcohol and 4.5 g of sodium hydroxide under the above described conditions we obtained 19 g (94%) of O-methyl O-butyl chlorothiophosphate.

B. p. 89-90° (9 mm), d_4^{20} 1.1828, n_D^{20} 1.4750.
Found %: P 14.9, 15.1; Cl 17.33. $C_5H_{12}O_2ClP$. Calculated %: P 15.3; Cl 17.5.

Preparation of O-methyl O-isoamyl chlorothiophosphate. From 20 g of isoamyl dichlorothiophosphate, 8 ml of methyl alcohol and 4.2 g of sodium hydroxide we obtained 17 g of O-methyl O-butyl chlorothiophosphate (87.5%).

B. p. 107-110° (16 mm), d_4^{20} 1.1259, n_D^{20} 1.4676.
Found %: P 14.3, 13.9; Cl 16.07, 16.24. $C_6H_{14}O_2ClP$. Calculated %: P 14.3; Cl 16.4.

SUMMARY

A simple method was developed for the preparation of dialkyl chlorothiophosphates by reacting phosphorus thiotrichloride or an alkyl dichlorothiophosphate with an alcohol in the presence of sodium hydroxide. The yields of dialkyl chlorothiophosphates by this method were 75-94% of the theoretical.

LITERATURE CITED

[1] G. Schrader, Progr. Chem. 22, 523 (1953).

[2] G. M. Kosolapoff, Organophosphor Compounds (New York, 1950).

[3] N. N. Melnikov, Progr. Chem. 22, 253 (1953).

[4] J. Fletcher, J. C. Hamilton, I. Hechenbleikner, E. Hoegberg, B. Sertl and J. T. Cassaday, J. Am. Chem. Soc. 70, 3943 (1948).

[5] N. N. Melnikov, Ya. A. Mandelbaum and K. D. Shvetsova-Shilovskaya, Author's Certificate No. 82206.

[6] British Patent No. 692169; C. A. 48, 10051 (1954).

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XXIV. NEW METHOD FOR THE PREPARATION OF HALOPHENYL ESTERS OF SULFONIC ACIDS

L. G. Volfson, S. D. Volodkovich, N. N. Melnikov and I. M. Rubleva

In recent years it was established that many esters of the aromatic sulfonic acids show quite strong acaricidal activity. Some of the sulfonic acid esters find practical use in agriculture for combatting harmful plant mites [1]. One of the esters of this type, finding practical utility, is the p-chlorophenyl ester of p-chlorobenzenesulfonic acid, known as "ovotran" in the foreign literature, and as sulfonate-ester in the Soviet literature. The sulfonate-ester and compounds similar to it are usually obtained by reacting the corresponding sulfonyl chlorides with phenolates in aqueous medium. However, due to the strong and disagreeable odor, it is quite inconvenient to work with the chlorophenols and dichlorophenols, especially since the pure p-chlorophenol is obtained only by the chlorination of phenol with sulfuryl chloride. In connection with the above we undertook a study of the chlorination of the phenol esters of sulfonic acids, since here the need of working with the chloro- and dichlorophenols is excluded. We studied the chlorination of the phenyl esters of sulfonic acids on the examples of preparing the chloro- and dichlorophenyl esters of methane-, benzene- and p-chlorobenzenesulfonic acids. Here we were able to establish that the first chlorine enters the para-position, and the corresponding p-chlorophenyl esters of the sulfonic acids are obtained in nearly quantitative yield. The introduction of the second chlorine proceeds at a considerably slower rate, while the trichloro derivatives cannot be obtained under the usual chlorination conditions. In the given case the same situation is observed as in the chlorination of the esters of carboxylic acids and of phenoxyacetic acid [2], with the only difference that in our case the chlorination proceeds at a slower rate and after the introduction of two chlorines is practically at a standstill.

Properties of the Halophenyl Esters of Methane-, Benzene- and p-Chlorobenzenesulfonic Acids

Formula	Yield (in %)	Melting point	Analysis for chlorine and sulfur (in %)			
			Cl		S	
			found	calculated	found	calculated
2-$ClC_6H_4OSO_2CH_3$	80	165—170° (17 mm) (b. p.)	16.91	17.14	—	—
4-$ClC_6H_4OSO_2CH_3$	70	65—66	16.78	17.14	15.10	15.50
2,4-$Cl_2C_6H_3OSO_2CH_3$	95	67—68	—	—	13.79	13.28
2-$ClC_6H_4OSO_2C_6H_5$	85	41—43	14.20	13.22	—	—
4-$ClC_6H_4OSO_2C_6H_5$	90	60	14.00	13.22	—	—
2,4-$Cl_2C_6H_3OSO_2C_6H_5$	95	54—55	—	—	10.40	10.59
2-$ClC_6H_4OSO_2C_6H_4Cl$	80	110—111	23.70	23.40	—	—
4-$ClC_6H_4OSO_2C_6H_4Cl$	98	83 *	23.57	23.40	—	—
2,4-$Cl_2C_6H_3OSO_2C_6H_4Cl$	95	106 **	—	—	8.55	9.48

*M. p. 85° according to [3].

**M. p. 118° according to [4].

For the purpose of comparing the properties of the isomeric compounds from sulfonyl chlorides and o-chlorophenol we synthesized the previously unknown o-chlorophenyl esters of the sulfonic acids. The compounds obtained by us and their properties are presented in the table.

EXPERIMENTAL

Chlorination of phenyl esters of sulfonic acids. The phenyl esters of methane-, benzene- and p-chlorobenzenesulfonic acids were chlorinated in the presence of iodine to the p-chlorophenyl esters at 90-100° and to the 2,4-dichlorophenyl esters at 130-140°, in which connection the temperature was raised to 130-140° only after one chlorine atom had been introduced. The obtained esters were purified by recrystallization from benzene. To identify the compounds the melting points of their mixtures with the corresponding chlorophenyl esters of methane-, benzene- and p-chlorobenzenesulfonic acids, obtained from the acid chlorides and phenolates of the pure chlorophenols, were determined. In addition, all of the compounds were analyzed for either halogen or sulfur.

Preparation of o-chlorophenyl esters of methane-, benzene- and p-chlorobenzenesulfonic acids. To a mixture of equimolar amounts of o-chlorophenol (obtained through the diazo compound from o-chloroaniline) and the sulfonyl chloride at 50-60° with good stirring was gradually added a 10% sodium hydroxide solution in water (an equivalent amount). The reaction mixture was stirred for 30 minutes, the resulting ester separated, and then purified either by vacuum distillation or by recrystallization. The properties of the esters are presented in the table.

SUMMARY

A new method was developed for obtaining the chlorophenyl esters of sulfonic acids. It was shown that in the chlorination of the phenyl esters of sulfonic acids the first chlorine atom enters the 4 position. A number of previously unknown sulfonic acid esters were synthesized.

LITERATURE CITED

[1] L. G. Volfson, S. D. Volodkovich and N. N. Melnikov, Trans. Sci. Research Inst. Fertilizers and Insecticides (State Chem. Press, Moscow, 1955), 154, 168.

[2] N. N. Melnikov, Yu. A. Baskakov and K. S. Bokarev, Chemistry of Herbicides and Plant Growth-Stimulants (State Chem. Press, Moscow, 1954).

[3] A. H. Kutschinsky and E. N. Luce, Anal. Chem. 24, 1188 (1952).

[4] H. R. Slagh and E. C. Britton, J. Am. Chem. Soc. 72, 2808 (1950).

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ORGANIC INSECTOFUNGICIDES

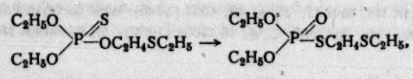
XXV. SYNTHESIS OF MIXED ESTERS OF THIOPHOSPHORIC ACID

Ya. A. Mandelbaum, N. N. Melnikov and V. I. Lomakina

In recent years a large number of different esters of phosphoric, thiophosphoric and dithiophosphoric acids have been described in the literature, some of which show strong insecticidal and acaricidal action and find extensive use for the control of plant pests [1]. Of the thio- and dithiophosphoric acid esters the compounds that show systemic action are of especial interest, which compounds are capable of traveling through the vascular system of plants and imparting to them for a variable length of time the ability to kill the pests that feed on their juices. A systemic insecticide that has found fairly extensive use is O,O-diethyl β-ethylmercaptoethyl thiophosphate, known under the names of "vnuran", "mercaptofos", "systox," "intox", etc. O,O-Diethyl β-ethylmercaptoethyl dithiophosphate and the homologs and analogs of the indicated esters have also been described [2]. However, there is not any information in the literature on the synthesis of esters that contain three different ester groups. Despite this, the synthesis of this type of thiophosphates is of undoubted interest, since a comparatively high insecticidal activity and lower toxicity for warm-blooded animals and humans could be expected from them.

In connection with the above we synthesized a number of O,O-dialkyl O-β-ethylmercaptoethyl thiophosphates with all three of the ester groups being different. The synthesis of these compounds was accomplished by starting from the mixed esters of chlorothiophosphoric acid, recently described by us [3], and β-hydroxydiethyl sulfide in the presence of sodium hydroxide. We synthesized the known O,O-dimethyl O-β-ethylmercaptoethyl thiophosphate in a similar manner, the preparation of which by other investigators was accomplished by more complicated routes. The compounds obtained by us and their properties are presented in the table. It is interesting to mention that in its insecticidal action the O-methyl O-ethyl O-β-ethylmercaptoethyl thiophosphate approaches that of O,O-diethyl O-β-ethylmercaptoethyl thiophosphate, but in its toxicity for warm-blooded animals it is considerably weaker than the latter.

When heated, all of the compounds synthesized by us are capable of transformation into the corresponding thiol isomers, as is the case for the O,O-dimethyl and O,O-diethyl O-β-ethylmercaptoethyl thiophosphates [4]:



with only the difference that in our case this reaction proceeds with somewhat greater difficulty. But when heated above 100° the isomerization proceeds violently.

EXPERIMENTAL

All of the compounds listed in the table were obtained under the following conditions: in a flask fitted with reflux condenser, thermometer, dropping funnel and efficient mechanical stirrer, making not less than 300 revolutions a minute, was placed a mixture of equimolar amounts of the dialkyl chlorothiophosphate and

Properties of Mixed Esters of Thiophosphoric Acid (Thiono Isomers)

Formula	Yield (%)	Boiling point (mm)	d_4^{20}	n_D^{20}	Analysis for P % found	Analysis for P % calculated
$(CH_3O)_2PSOCH_2CH_2SC_2H_5$	68	79° (0.1)	1.1848	1.4980		
$CH_3O\diagdown\!\!\!\!\diagup S$ $POCH_2CH_2SC_2H_5$ $C_2H_5O\diagup$	80	80—82 (0.1)	1.1526	1.4930	12.6, 12.7	12.9
$CH_3O\diagdown\!\!\!\!\diagup S$ $POCH_2CH_2SC_2H_5$ iso-$C_3H_7O\diagup$	45	88—92 (0.05)	1.1434	1.4870	12.0, 11.9	12.0
$CH_3O\diagdown\!\!\!\!\diagup S$ $POCH_2CH_2SC_2H_5$ $C_4H_9O\diagup$	79	86 (0.25)	1.1105	1.4930	10.9	11.7
$CH_3O\diagdown\!\!\!\!\diagup S$ $POCH_2CH_2SC_2H_5$ iso-$C_5H_{11}O\diagup$	47	125—130 (0.13)	1.0842	1.4980	11.1, 10.9	10.8

β-hydroxydiethyl sulfide, and after cooling to −12° a saturated aqueous solution of sodium hydroxide (or powdered sodium hydroxide) was added. The temperature during the sodium hydroxide addition should not exceed 0°. On conclusion of adding the sodium hydroxide the reaction mixture was kept with good stirring at 15-20° for 2.5-3 hours and at 40-65° for 30-90 minutes. The reaction mixture after cooling was diluted with water, and after standing, the oil layer of the ester was separated, washed with water, and after drying over anhydrous calcium chloride, was vacuum distilled. The vacuum distillation should be done very carefully, as overheating leads to violent isomerization to the thiol isomer.

SUMMARY

A number of previously unknown mixed esters of thiophosphoric acid were synthesized, containing three different ester groups. Some of the synthesized compounds show the properties of systemic insecticides.

LITERATURE CITED

[1] G. Schrader, Progr. Chem. 22, 523 (1953); N. N. Melnikov, Progr. Chem. 22, 253 (1953).

[2] West German Patent No. 850677; C. A. 47, 4034 (1953); West German Patent No. 917668; Chem. Zentr. 1955, 4440; U. S. Patent No. 2571989; C. A. 46, 3066 (1952); U. S. Patent No. 2597534; C. A. 47, 4357 (1953).

[3] N. N. Melnikov, Ya. A. Mandelbaum, V. I. Lomakina and Z. M. Bakanova, J. Gen. Chem. 26, 2577 (1956) (T. p.

[4] T. R. Fukuto and R. L. Metcalf, J. Am. Chem. Soc. 76, 5103 (1954); A. Henglein and G. Schrader, Z. Naturforsch. 10b, 12 (1955).

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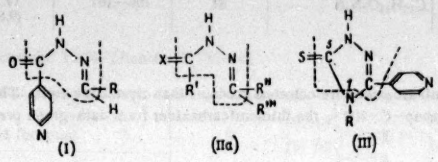
*T. p. = C. B. Translation pagination.

ON HETEROCYCLIC COMPOUNDS OBTAINED FROM HYDRAZIDES

I. 1,3,4-TRIAZOLE-5-THIONES

I. Ya. Postovsky and N. N. Vereshchagina

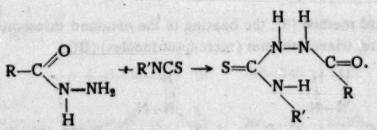
A large number of isonicotinoyl hydrazones (I) have been described in recent years, among which highly active tuberculostatic compounds have been found [1, 2]. According to the data of M. N. Shchukina and co-authors [1] the grouping $=C-N-N=C-$ (II) plays a role in the development of the tuberculostatic properties of these compounds, which grouping is also present in a number of other highly active antitubercular compounds (thiosemicarbazone derivatives, phthalazones, etc.). Other authors [2], indicating the role played by grouping (II), attach greater importance to the structure of the radicals R', R", R"' (IIa), since it was found that the activity of the compounds depends to a considerable degree on the nature of these radicals, in which connection the greatest activity is observed for the compounds where R"' corresponds to the γ-pyridyl radical.



(I) (IIa) (III)

In this paper we communicate on the synthesis of several 1,3,4-triazole-5-thiones (III). In these compounds the (II) grouping is found in a ring having the γ-pyridyl radical as one of the substituents. There is very little information in the literature on similar cyclic compounds [3], although a study of their tuberculostatic activity is of considerable interest for elucidation of the relationship existing between antibacterial action and chemical structure.

The starting materials for the synthesis of the triazoles were the 1-acyl-4-aryl-substituted thiosemicarbazides, which were obtained by reacting isonicotinic hydrazide with the corresponding isothiocyanates in accord with the scheme:



Compounds (IV-VI) were synthesized, where: R is the pyridyl radical, while R' in (IV) is p-C_6H_4Cl, in (V) it is p-$C_6H_4OCH_3$, and in (VI) it is p-$C_6H_4OC_2H_5$.

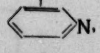
In addition to these thiosemicarbazides, for a comparison of properties we also synthesized the thiosemicarbazides that were obtained from the hydrazides of other acids, like nicotinic (VII), benzoic (VIII) and p-aminobenzoic (IX) acids, where: R' is always equal to p-$C_6H_4OC_2H_5$, while R in (VII) is  in (VIII) is C_6H_5, and in (IX) is p-$C_6H_4NH_2$. These thiosemicarbazides were also converted into triazoles. The yields, melting points and analysis results of the disubstituted thiosemicarbazides are given in Table 1.

TABLE 1

1,4-Substituted Thiosemicarbazides

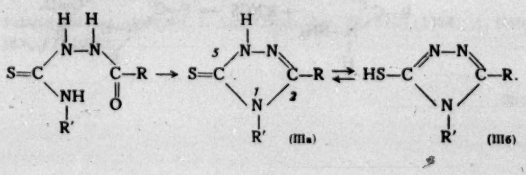
Compound Nos.	Empirical formula	Yield (in %)	Melting point •	Amount of nitrogen (sulfur) (in %)	
				found	calculated
(IV)	$C_{13}H_{11}ON_4SCl$ . . .	91	179—180° (from alcohol)	18.12	18.30
(V)	$C_{14}H_{14}O_2N_4S$	92	177—178	18.61	18.54
(VI)	$C_{15}H_{16}O_2N_4S$	94	175—177	17.54	17.72
(VII)	$C_{15}H_{16}O_2N_4S$	90	160—161	17.45	17.72
(VIII)	$C_{16}H_{17}O_2N_3S$	86	166—167	12.64 (9.99)	13.33 (10.10)
(IX)	$C_{16}H_{18}O_2N_4S$	87	166—167	17.51 (9.81)	16.96 (9.60)

• Uncorrected.

The obtained thiosemicarbazides are colorless products that crystallize well. The same as compounds containing the thioamide group $-C(=S)-NH-$, the thiosemicarbazides form dark-green precipitates with Cu^{2+} salts. The ability to form Cu salts (or complexes [4]) is considered to be characteristic for many tuberculostatic compounds, for which reason it could be expected that the obtained thiosemicarbazides will also show antitubercular activity.

After the present study had already been completed, a paper appeared by Buu-Hoi and co-authors [5], in which some substituted thiosemicarbazides were described as being antitubercular compounds; among them were included three of our synthesized thiosemicarbazides (V), (VI) and (VII). Proceeding from the in vitro tests, Buu-Hoi considers the disubstituted thiosemicarbazides as being a new group of active antitubercular compounds. In contrast to these data, the disubstituted thiosemicarbazides synthesized by us, including those presented by Buu-Hoi as being examples of active compounds (V, VI, VII), proved in the in vitro experiments to be inactive toward the tubercle bacillus (human strain K_1).

Using the Girard method [6], the heating of the obtained thiosemicarbazides (Table 1) with dilute alkali gave the corresponding triazolethiones (mercaptotriazoles) (III):



(IIIa) (IIIб)

These compounds are colorless substances that crystallize well from alcohol. They dissolve in alkali and give either dark-green precipitates or solutions with Cu^{2+} salts. The reaction of some of the triazoles with Cu^{2+} is quite sensitive; thus, for example, compound (XII) gives a distinctly colored solution even with a copper content of 10^{-5} g/ml.

The obtained compounds are characterized in Table 2.

All of the triazoles (X-XV) are readily soluble in alkali, give precipitates with heavy metal salts, and evidently react as mercapto compounds (IIIb).

The obtained triazoles belong to the class of heterocyclic compounds that contain the thiol grouping $-C(SH)=N-$, capable of tautomeric transformations into the thiono (thioamide) group $-C(=S)-NH-$. As a rule, this type of compounds, as follows from the infrared absorption spectra, appear as thiones in the crystalline state. For example, this is known for 2-mercaptobenzothiazole [7], 2-mercaptothiazoline [7] and other similar heterocyclic compounds containing the SH-group [8].

We investigated the IR spectra of three of the obtained compounds (X, XII, XIV) in the crystalline state.* The spectra of these compounds failed to show the bands characteristic for the valence oscillation of the SH group (2500 cm^{-1}) [9], for which reason distinct bands were revealed for the NH (in the 3300-3100 cm^{-1} region) and C=S (in the 1500-1516 cm^{-1}) groups [10]. As a result, in the crystalline state the examined compounds have the structure of thiones (thioamides) (IIIa). It must be assumed that the other triazole compounds (XI, XIII, XV) described in this paper also have a thione (thioamide) structure in the crystalline state. For this reason it will be expedient to consider and record these compounds as being 1,3,4-triazole-5-thiones.

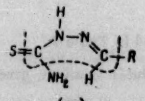
TABLE 2

1-R', 2-R-Substituted 1,3,4-Triazole-5-Thiones

Compound Nos.	Empirical formula	R	R'	Yield (in %)	Melting point	Amount of nitrogen (in %) found	Amount of nitrogen (in %) calculated
(X)	$C_{13}H_9N_4SCl$		n-C_6H_4Cl	87	269—271° (from alcohol)	19.30	19.41
(XI)	$C_{14}H_{12}ON_4S$		n-$C_6H_4OCH_3$	87	238—239	19.66	19.72
(XII)	$C_{15}H_{14}ON_4S$		n-$C_6H_4OC_2H_5$	90	223—224	18.62	18.79
(XIII)	$C_{15}H_{14}ON_4S$		n-$C_6H_4OC_2H_5$	87	238—240	18.80	18.79
(XIV)	$C_{16}H_{15}ON_3S$	C_6H_5	n-$C_6H_4OC_2H_5$	87	264—265	14.07	14.14
(XV)	$C_{18}H_{16}ON_4S$	p-$C_6H_4NH_2$	n-$C_6H_4OC_2H_5$	80	268—269	17.71	17.91

* We are indebted to Yu. N. Sheinker (All-Union Sci-Res. Chem.-Pharm. Institute) and L. F. Trefilova for taking the IR spectra.

As indicated above, in the thiono form these compounds (IIIa) have the atomic grouping (II), found in tuberculostatic compounds. In addition, in the thiono form these compounds represent, as it were, cyclic analogs of thiosemicarbazones (XVI).



(XVI)

Thiosemicarbazone (XVI), in which R corresponds to the γ-pyridyl radical, is known as a highly active tuberculostatic compound [11]. All of this, and also the above mentioned capacity to form complexes with Cu salts, gave reason to assume that the synthesized triazolethiones will possess antitubercular activity, especially compounds (X, XI, XII), containing the γ-pyridyl radical. However, in the in vitro experiments it was established that the obtained triazolethiones fail to suppress growth of the tubercle bacillus to any significant degree.

In conclusion we take this occasion to thank E. I. Chertkova (Sverdlovsk Scientific Research Tuberculosis Institute) for making the numerous microbiological tests.

EXPERIMENTAL

Preparation of 1-isonicotinoyl-4-(p-chlorophenyl) thiosemicarbazide (IV). To a hot solution of 3.7 g (0.027 mole) of isonicotinic hydrazide in 60 ml of alcohol was added a hot solution of 4.4 g (0.027 mole) of p-chlorophenyl isothiocyanate. Here the color of the solution turned bright red. After several minutes colorless plates deposited. The precipitate after cooling was filtered and washed several times with alcohol. Weight 7.5 g (91%). The substance is soluble in alkali, and insoluble in the cold in acetone, benzene and chloroform. It gives a light-yellow color with dilute sulfuric acid. Compounds (V-IX) were obtained in a similar manner. The melting points given in the literature for compounds (V-VII) are higher than those obtained by us. The constant melting points are indicated in Table 1; repeated analyses confirmed the purity of the substances. Apparently, the differences from the literature data are connected with the use of different methods to determine the melting points.

Preparation of 1-(p-chlorophenyl)-2-(γ-pyridyl)-1,3,4-triazole-5-thione (X). A solution of 0.5 g of 1-isonicotinoyl-4-(p-chlorophenyl) thiosemicarbazide in 6 ml of 2N NaOH was boiled for 15 minutes. A precipitate of the Na salt deposited on cooling. The precipitate was filtered and then dissolved in a small amount of water, after which the water solution was treated with concentrated hydrochloric acid until weakly acid to litmus. The white precipitate obtained here was filtered and washed with water. Weight 0.4 g (87%). The substance is insoluble in benzene and chloroform, difficultly soluble in acetone, and readily soluble in hot alcohol and in cold alkali. It dissolves in dilute sulfuric acid with a yellow color. Compounds (XI-XV) were obtained in a similar manner. The melting points of the compounds and the analysis results are given in Table 2.

The thiosemicarbazides and triazoles were reacted with metal salts in the following manner. To 1 ml of a 1N solution of the metal salt was added several drops of a 0.25% solution of the substance in alcohol.

Spectroscopic Study. The infrared absorption spectra of compounds (X, XII, XIV) were taken on an IKS-11 recording spectrometer, using an LiF prism in the 2.5-4.5 μ region and a NaCl prism in the 4.5-7.5μ region. The substances were photographed as fine suspensions with perfluorohydrocarbons. None of the spectra of the compounds showed an absorption band in the 2700-2400 cm^{-1} region (absorption bands, corresponding to the characteristic vibration of the −SH group, lie in the 2500-2570 cm^{-1} region). As already indicated above, the thioamide structure of the investigated compounds was supported by the presence of bands corresponding to the vibrations of the NH- and C=S-groups.

Compound Nos.	Revealed absorption bands (in cm^{-1}) of the corresponding groups	
	C=S	NH
(X)	1500 (weak)	3130 (weak)
(XII)	1514 (strong)	3388 (strong)
(XIV)	1516 (strong)	3440 (strong)
		3075 (average)

SUMMARY

1. The reaction of the hydrazides of isonicotinic, nicotinic, benzoic and p-aminobenzoic acids with mustard oils gave 1-acyl-4-aryl-substituted thiosemicarbazides (IV-IX).

2. The heating of these thiosemicarbazides with dilute alkali gave a number of new cyclic compounds – the 1,2-substituted 1,3,4-triazole-5-thiones (X-XV).

3. On the basis of studying the IR spectra of compounds (X, XII, XIV) in the crystalline state a thiono (thioamide) structure (IIIa) is assumed for triazoles. The triazoles react like mercapto compounds with alkalies and with heavy metal salts.

4. The synthesized compounds – thiosemicarbazides (IV-IX) and triazoles (X-XV) – fail to show tuberculostatic properties.

LITERATURE CITED

[1] M. N. Shchukina, G. N. Pershin, O. O. Makeeva, E. D. Sazonova, E. S. Nikitskaya, A. D. Yanina and A. I. Yakovleva, Proc. Acad. Sci. USSR 84, 981 (1952).

[2] H. A. Offe, W. Siefken and G. Domagk, Chem. Zentr. 1953, 8897; H. H. Fox and J. T. Gibas, J. Org. Chem. 18, 983 (1953); O. Efimovsky and P. Rumpf, Bull. soc. chim. 1954, 1401; D. Liebermann et al., Bull. soc. chim. 1954, 1430.

[3] F. McMillan et al., J. Am. Pharm. Assoc. 42, 457 (1953); H. König, W. Siefken and H. A. Offe, Ber. 87, 826 (1954).

[4] E. Carl and P. Marquardt, C. A. 44, 3157 (1950).

[5] N. P. Buu-Hoi, Ng. D. Xuong and Ng. H. Nam, Compt. rend. 238, 295 (1954).

[6] M. Girard, Compt. rend. 225, 458 (1947).

[7] M. C. Flett, J. Chem. Soc. 1953, 347.

[8] H. Culbertson, J. C. Decius and B. E. Christensen, J. Am. Chem. Soc. 74, 4834 (1952).

[9] V. M. Chulanovsky, Introduction to Molecular Spectral Analysis (State Tech. and Theor. Lit. Press, 1951), pp. 377-385 (tables).

[10] H. M. Randall, et al., Infrared Determination of Organic Structures (Van Nostrand Company, New York, 1951).

[11] H. H. Fox, J. Org. Chem. 17, 555 (1952).

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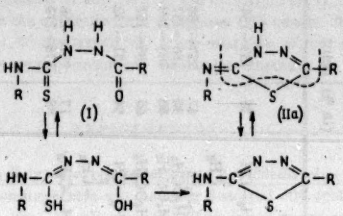
ON HETEROCYCLIC COMPOUNDS OBTAINED FROM HYDRAZIDES

II. 2,5-SUBSTITUTED 1,3,4-THIADIAZOLES

N. N. Vereshchagina and I. Ya. Postovsky

In the previous paper [1] we had described some 1-isonicotinoyl-, 1-nicotinoyl- and other 1-acyl-, 4-aryl-substituted thiosemicarbazides, which when heated with alkali gave 1,2-substituted 1,3,4-triazole-5-thiones in good yield. In the present study, starting from 1-isonicotinoyl- and other 1-acyl-4-allyl- and aryl-substituted thiosemicarbazides (I), we synthesized a number of heterocyclic compounds, and specifically, the 2,5-substituted 1,3,4-thiadiazoles (II):

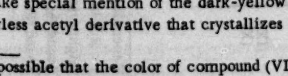


In the tautomeric form (IIa) such compounds have the $=C-N-N=C-$ grouping (shown by a dotted line).

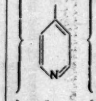
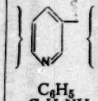
According to the data of M. N. Shchukina and co-authors [2], the antitubercular activity of a whole series of compounds is associated with the presence of this grouping.

In their time the 2,5-substituted thiadiazoles were obtained by reacting acetyl chloride with either 1-acyl-4-alkyl- or aryl-substituted thiosemicarbazides [3]. More convenient is the method of [4], where 1-acyl-thiosemicarbazides can easily be converted into thiadiazoles by treatment with concentrated sulfuric acid in the cold. With this method we obtained a number of thiadiazoles in 35 to 70% yield. Only in the case of 1-benzoyl-4-(p-ethoxyphenyl) thiosemicarbazide were we unable to effect ring closure with this method. Here the thiadiazole compound (IX) was always obtained when the thiosemicarbazide was reacted with acetyl chloride.

The obtained thiadiazoles are either colorless (III, VII, VIII, IX) or yellow compounds (IV, V, VI, X). We make special mention of the dark-yellow color of compound (VI). The acetylation of this compound gives a colorless acetyl derivative that crystallizes well.*

*It is possible that the color of compound (VI) is associated either with transition into the tautomeric quinoid form  or with the formation of intermolecular compounds.

2-R, 5-NHR'-, 1,3,4-Thiadiazoles

Compound Nos.	Empirical formula	R	R'	Yield (in %)	Melting point	Nitrogen content (in %) found	Nitrogen content (in %) calculated	Color of luminescence in the crystalline state	Color of luminescence in alcohol solution
(III)	$C_{10}H_{10}N_4S$		$-CH_2-CH=CH_2$	76	133—134°	25.50	25.68	Bright-violet	Bright-violet
(IV)	$C_{13}H_9N_4SCl$		p-C_6H_4Cl	47	257—258	19.40	19.41	Violet	Pale yellow
(V)	$C_{14}H_{12}ON_4S$		p-$C_6H_4OCH_3$	50	186—187	19.68	19.72	Yellow-green	Yellow
(VI)	$C_{15}H_{14}ON_4S$		p-$C_6H_4OC_2H_5$	60	188—189	18.50	18.79**	Not luminescent	Yellow
(VII)	$C_{15}H_{14}ON_4S$		p-$C_6H_4OC_2H_5$	66	185—187	18.44	18.79***	Not luminescent	Yellow
(VIII)	$C_{10}H_{10}N_4S$		$-CH_2-CH=CH_2$	54	131—132	25.95	25.68	Not luminescent	Bright-violet
(IX)	$C_{16}H_{15}ON_3S$	C_6H_5	p-$C_6H_4OC_2H_5$	17	157—158	13.96	14.14	Light-blue	Not luminescent
(X)	$C_{16}H_{16}ON_4S$	p-$C_6H_4NH_2$	"	38	178—179	17.83	17.91	Bright-azure	Violet

*Depending on the pH of the medium, the substances given in the table show a change in the color of their luminescence. The change in the color of luminescence is especially distinct for compound (III), which at pH below 3.2 shows a turquoise luminescence, which turns to a bright-violet at pH above 3.8.

**Found %: S 10.62; Calculated %: S 10.73.

***Found %: S 10.87; Calculated %: S 10.73.

In contrast to the starting thiosemicarbazides the thiadiazoles are insoluble in alkali; however, alcohol solutions of the thiadiazoles give with some metal salts, for example with Cu^{2+} salts, either precipitates or colored solutions. Also characteristic for the obtained thiadiazoles is their bright luminescence in the filtered ultraviolet of a quartz lamp. The synthesized compounds are presented in the table.

In studying the tuberculostatic properties, made at our request by E. I. Chertkova, it was revealed that the synthesized 2,5-substituted thiadiazoles are inactive compounds. Apparently, inclusion of the $=C-\overset{H}{\underset{|}{N}}-H=C-$ grouping in the ring leads to the complete removal of tuberculostatic properties. We observed

a similar negative cyclization effect earlier in comparing the active p-acetylaminobenzalthiosemicarbazone and its inactive cyclic analog 2-amino-(5-p-acetamidophenyl)-1,3,4-thiadiazole [5].

The results of investigating the tuberculostatic properties of the compounds, synthesized in this and previous studies, also suggest that the $=C-\overset{C}{\underset{|}{N}}-H=C-$ grouping, even in the presence of a γ-pyridyl radical in the molecule, is very rarely sufficient to assure antitubercular activity. Only in isolated cases, in definite combination with other structural characteristics, can it show significance for the manifestation of this activity. Evidently, in contradiction to the opinions of Buu-Hoi [6] and other authors [7], it is also not possible to associate antibacterial activity only with the ability to form complexes with metals. This was already indicated recently by M. N. Shchukina and N. V. Savitskaya [8]. In our case also, as can be seen from the data given above, the ability to give compounds with copper proved an insufficient condition for the manifestation of tuberculostatic action.

EXPERIMENTAL

Preparation of 2-(γ-pyridyl)-5-(p-ethoxyphenylamino)-1,3,4-thiadiazole (VI). Two grams of 1-isonicotinoyl-4-(p-ethoxyphenyl) thiosemicarbazide was gradually dissolved with cooling in 10 ml of concentrated sulfuric acid. The solution stood for 15 minutes, after which it was poured over ice. Here the thiadiazole sulfate was obtained as a red precipitate, which when treated with ammonia until alkaline was converted into the yellow base. The precipitate of the base was filtered, washed with water, and then recrystallized from alcohol. Bright yellow plates with m. p. 188-189° were obtained. Weight 1.4 g (60 %). The substance is insoluble in the cold in acetone, chloroform and benzene. It dissolves in strong sulfuric acid with the formation of a red color. The addition of an alcohol solution of the thiadiazole to a water solution of $FeSO_4$ gives an orange precipitate, while reaction with $CuCl_2$ solution gives a green precipitate at first, which quickly changes to a light-brown, and reaction with $CuSO_4$ solution gives a dark-yellow precipitate. The blue color of its solution with vanadyl sulfate changes to a khaki, and after some time a bright-orange precipitate deposits from solution. Product (VI) and the other compounds described here can be of interest for further study as possible analytical reagents.

The acetyl derivative was obtained in nearly quantitative yield by heating the product with acetic anhydride. It crystallizes from aqueous alcohol as colorless needles with m. p. 192-193°.

Found %: N 16.32. $C_{17}H_{16}O_2N_4S$. Calculated %: N 16.47.

Compounds (III, IV, V, VII, VIII, X) were obtained in a manner similar to compound (VI) from the corresponding thiosemicarbazides.

Preparation of 2-phenyl-5-(p-ethoxyphenylamino)-1,3,4-thiadiazole (IX). To 1 g of 1-benzoyl-4-(p-ethoxyphenyl)-thiosemicarbazide was added 7 ml of acetyl chloride and the mixture was allowed to stand at room temperature. The precipitate began to dissolve gradually, and the solution assumed a yellow color. After all of the precipitate had dissolved the reaction mass was poured over ice. After some time a yellow oily precipitate was obtained, which turned to a white color when ammonia was added until alkaline. The precipitate

was filtered and washed with water. Weight 0.7 g. The substance melts over a wide range. After 3-4 recrystallizations from aqueous alcohol we were able to isolate 0.1 g (1%) of product with constant m. p. 157-158°. (See Table for analysis).

SUMMARY

1. The reaction of 1-acyl-4-allyl- and aryl-substituted thiosemicarbazides with strong sulfuric acid gave eight new 2,5-substituted 1,3,4-thiadiazoles.

2. The obtained thiadiazoles fail to possess tuberculostatic properties.

LITERATURE CITED

[1] I. Ya. Postovsky and N. N. Vereshchagina, J. Gen. Chem. 26, 2583 (1956) (T. p. 2879).*

[2] M. N. Shchukina, G. N. Pershin, O. O. Makeeva, E. O. Sazonova, E. S. Nikitskaya, A. D. Yanina and A. I. Yakovleva, Proc. Acad. Sci. USSR 84, 981 (1952).

[3] L. Pulvermacher, Ber. 27, 613 (1894); M. Freund, Ber. 28, 2483 (1895); W. Marckwald and A. Bott, Ber. 29, 2916 (1896).

[4] M. Ohta and H. Koyama, C. A. 47, 9324 (1953).

[5] F. F. Medovshchikova and I. Ya. Postovsky, J. Gen. Chem. 24, 2024 (1954) (T. p. 1989).*

[6] N. P. Buu-Hoi, F. Binon and Ng. Hoan, Compt. rend. 235, 329 (1952).

[7] C. Sorkin and W. Ross, Helv. Chim. Acta 34, 427 (1951); E. Carl and P. Marquardt, Z. Naturforsch. 4, 280 (1949); 7, 575 (1952).

[8] M. N. Shchukina and N. V. Savitskaya, J. Gen. Chem., 22, 1218, 1224 (1952) (T. p. 1269).*

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*T. p. = C. B. Translation pagination.

SUBSTITUTED HYDRAZIDES OF HYDROXYCARBOXYLIC ACIDS

I. SYNTHESIS OF ARYLHYDRAZIDES OF DIARYLGLYCOLIC ACIDS

I. S. Berdinsky and P. A. Petyunin

In recent years considerable interest has been shown in hydrazides of acids and their derivatives, due to the fact that some of them proved to be active as antitubercular compounds [1]. The known antitubercular compound "Phthivazide" is one of the derivatives of isonicotinic hydrazide [2]. The discovery of antitubercular activity for the indicated group of compounds led to numerous studies of extremely different carboxylic acid hydrazides and their derivatives. Thus, antitubercular activity was established for the hydrazides of p-hydroxybenzoic acid, α- naphthalenecarboxylic acid [3], benzoic acid [4], etc. In this respect it seemed of interest to us to study the arylhydrazides of the diarylglycolic acids. However, the latter have been left completely unstudied, which is probably explained by the absence of an accessible method for their preparation. The known phenylhydrazide of benzilic acid was obtained by reacting phenylhydrazine with benzilic acid azide [5]. The direct reaction of phenylhydrazine with α-hydroxy acids or their esters does not always lead to the formation of the corresponding hydrazides. In a number of cases the esters of hydrazino acids are formed here [6, 7]. Due to the difficult availability of many α-hydroxy acids it is quite clear that the indicated method cannot find extensive use for the synthesis of the corresponding arylhydrazides.

Our task was to develop a more convenient method for obtaining the arylhydrazides of diarylglycolic acids and to study their properties. Our method for obtaining the arylhydrazides of diarylglycolic acids was based on the following reaction:

$$Ar{-}NH{-}NH{-}CO{-}COOC_2H_5 \xrightarrow[-C_2H_5OMgX]{+2RMgX} Ar{-}NH{-}NH{-}CO{-}\underset{\displaystyle OMgX}{\overset{\displaystyle |}{C}}R_2 \longrightarrow$$

$$\xrightarrow{+H_2O} Ar{-}NH{-}NH{-}CO{-}\underset{\displaystyle OH}{\overset{\displaystyle |}{C}}R_2,$$

where: Ar = C_6H_5-, p-BrC_6H_4-, β-$C_{10}H_7-$, $(C_6H_5)_2$=
R = C_6H_5-, p-$CH_3C_6H_4-$, $C_6H_5CH_2-$, α-$C_{10}H_7-$, o-$CH_3OC_6H_4-$.

The ethyl esters of the oxalic acid β-arylhydrazides (I-IV) needed for reaction were obtained by reacting arylhydrazines with diethyl oxalate in alcohol medium. Experimentation revealed that the reaction proceeds smoothly and the arylhydrazides of the diarylglycolic acids are obtained in 50-60% yield, based on recrystallized product. This makes it possible to recommend the reaction between the esters of oxalic acid hydrazides and arylmagnesium halides as being a preparative method for obtaining the arylhydrazides of diarylglycolic acids. The structural formulas of the compounds obtained by us are presented in the table. The arylhydrazides are colorless crystalline compounds, insoluble in water, and soluble in most organic solvents. With the exception of (IX), they give colored solutions with concentrated sulfuric acid.

Compound Nos.	Formula	Melting point	
		our data	literature data
(V)		143—144°	139—141 [5]
(VI)		168—169	—
(VII)		139—140	—
(VIII)		212° (with decompn.)	
(IX)		210—211	—
(X)		165—167	—
(XI)		201—203	—
(XII)		179—181	—

EXPERIMENTAL

Ethyl oxalate β-phenylhydrazide (I). A mixture of 50 g of diethyl oxalate and 30 g of phenylhydrazine in 50 ml of alcohol was allowed to stand for 2 days. Yield 30 g (51.9%). M. p. 119°. According to [8]: m. p. 119°.

Ethyl oxalate p-bromophenylhydrazide (II). a) To a solution of 5 g of ethyl oxalate β-phenylhydrazide in 15 ml of glacial acetic acid was added a solution of 4 g of bromine in 5 ml of glacial acetic acid. The reaction mass was heated on the water bath for 30 minutes, and after cooling, was poured into 75 ml of water. The resulting flocculent precipitate was filtered and purified by recrystallization from alcohol. Yield 2 g (28.9 %).

b) A mixture of 11 g of p-bromophenylhydrazine and 10 g of diethyl oxalate in 40 ml of alcohol was boiled for 1.5 hours. The secondary product – oxalic acid di(p-bromophenylhydrazide) – that separated here was filtered from the hot solution. M. p. 240° (with decomp.) [9]. The main reaction product separated from the filtrate on cooling. Yield 9 g (53.3%). Needles (from alcohol), m. p. 155-156°.

Found %: N 9.97, 10.02. $C_{10}H_{11}O_3N_2Br$. Calculated %: N 9.76.

Ethyl oxalate β-naphthylhydrazide (III) was obtained, as described above, from β-naphthylhydrazine* and diethyl oxalate [10]. Yield 34.6%. M. p. 159°.

Ethyl oxalate β,β-diphenylhydrazide (IV). a) Obtained by the method of [12]. Yield 28.3 %. Needles (from dilute alcohol), m. p. 129-131°. b) A mixture of 15 g of diphenylhydrazine** and 15 g of diethyl oxalate in 15 ml of alcohol was heated on the water bath for 5 hours. The small amount of oxalic acid di(β,β-diphenylhydrazide) obtained here was removed by filtration. The main reaction product was isolated by diluting the filtrate with water. Yield 6 g (26%). Needles (from alcohol), m. p. 130-131.5°.

*Obtained by the method of [11]. Yield 45.3 percent. M. p. 124-125°.

**The diphenylhydrazine was synthesized by the method of E. Fischer [13].

Benzilic acid phenylhydrazide (V). To a solution of phenylmagnesium bromide, prepared from 30.7 g of bromobenzene and 4.9 g of magnesium, was added 6.3 g of (I). The reaction mass was heated on the water bath for 20 minutes and then decomposed with dilute hydrochloric acid. The ether layer was separated and to remove the solvent, and also volatile reaction products, was steam-distilled. Yield 6 g (57.5%). Plates (from toluene), m. p. 143-144°. It gives a cherry-red color with concentrated sulfuric acid. From [5]: m. p. 139-141°.

Found %: C 75.23; H 5.66; N 8.76. $C_{20}H_{18}O_2N_2$. Calculated %: C 75.47; H 5.66; N 8.80.

p-Tolilic acid phenylhydrazide (VI). Starting substances: 6.8 g of (I), 4.9 g of magnesium and 33.4 g of p-bromotoluene. Yield 6.6 g (58.4%). Difficultly soluble in ether, and more readily soluble in alcohol, toluene and glacial acetic acid. Gives a red color with concentrated sulfuric acid. Fine needles (from toluene), m. p. 168-169°.

Found %: N 8.40, 8.19. $C_{22}H_{22}O_2N_2$. Calculated %: N 8.09.

Di-o-anisylglycolic acid phenylhydrazide (VII). We took for reaction: 4.8 g of (I), 3.3 g of magnesium and 32 g of o-iodoanisole. Yield 3.9 g (44.8%). Soluble in ether, alcohol, toluene and glacial acetic acid. Gives a green color with concentrated sulfuric acid. Needles (from toluene), m. p. 139-140°.

Found %: N 7.13, 7.27. $C_{22}H_{22}O_4N_2$. Calculated %: N 7.41.

Di-α-naphthylglycolic acid phenylhydrazide (VIII). Reaction was between 6.2 g of (I) and the α-naphthylmagnesium bromide obtained from 37.2 g of α-bromonaphthalene and 4.3 g of magnesium in 120 ml of ether. Yield 6 g (38.9%). Insoluble in water and ether, and soluble in alcohol, toluene and glacial acetic acid. Gives a blue color with concentrated sulfuric acid. Needles (from toluene), m. p. 212° (with decomp.).

Found %: N 6.59, 6.48. $C_{28}H_{22}O_2N_2$. Calculated %: N 6.69.

Dibenzylglycolic acid phenylhydrazide (IX). For reaction we took: 4.2 g of (I), 2.9 g of magnesium and 15.2 g of benzyl chloride. Yield 3.1 g (44.3%). Insoluble in water, and soluble in toluene, alcohol and benzene. Needles (from toluene), m. p. 210-211°.

Found %: N 7.77, 8.24. $C_{22}H_{22}O_2N_2$. Calculated %: 8.09.

Benzilic acid p-bromophenylhydrazide (X). Starting substances: 1.45 g of (II), 4.7 g of bromobenzene and 0.7 g of magnesium. Yield 0.9 g (45%). Insoluble in water and benzine, and soluble in alcohol, glacial acetic acid and toluene. Gives a red color with concentrated sulfuric acid. Prisms (from toluene), m. p. 165-167°.

Found %: N 7.29, 7.28. $C_{20}H_{17}O_2N_2Br$. Calculated %: N 7.05.

Benzilic acid β-naphthylhydrazide (XI). Reaction was between 3.9 g of (III) and the phenylmagnesium bromide obtained from 2.4 g of magnesium and 15.7 g of bromobenzene. Yield 3.5 g (62.5%). Insoluble in water and ether, and soluble in toluene, alcohol and glacial acetic acid. Gives a blue color with concentrated sulfuric acid. Needles (from glacial acetic acid), m. p. 201-203°.

Found %: N 7.49, 7.52. $C_{24}H_{20}O_2N_2$. Calculated %: N 7.61.

Benzilic acid β,β-diphenylhydrazide (XII). For reaction we took: 4 g of (IV), 2 g of magnesium and 13 g of bromobenzene. Yield 3.5 g (62.5%). Insoluble in water, difficultly soluble in ether, and more readily soluble in alcohol, toluene and glacial acetic acid. Gives a blue color with concentrated sulfuric acid. Prisms (from alcohol), m. p. 179-181°.

Found %: N 7.38, 7.22. $C_{26}H_{22}O_2N_2$. Calculated %: N 7.11.

SUMMARY

A preparative method was developed for obtaining the arylhydrazides of diarylglycolic acids. A number of previously unknown members of this group of compounds were prepared and their properties studied.

LITERATURE CITED

[1] I. Ya. Postovsky and S. I. Omelchenko, Progr. Chem. 23, 199 (1954).

[2] M. N. Shchukina, G. N. Pershin, O. O. Makeeva, E. D. Sazonova, E. S. Nikitskaya, A. D. Yanina and A. I. Yakovleva, Proc. Acad. Sci. USSR 84, 981 (1952).

[3] N. P. Buu-Hoi, M. Welsch, G. Dechamps, H. L. Bihan, F. Binon and C. Mentzer, Compt. rend. 234, 1925 (1952).

[4] M. Claesen, P. van Dijck and H. Vanderhaeghe, J. Pharm. and Pharmacol. 6, 127 (1954).

[5] Curtius, J. prakt. Chem. (2) 95, 205 (1917).

[6] E. Fischer and Passmore, Ber. 22, 2729 (1889).

[7] Reissert and Kayser, Ber. 22, 2928 (1889).

[8] Thiele-Schleussner, Ann. 295, 167 (1897).

[9] Wislicenus and Berg, Ber. 41, 3766 (1908).

[10] Freund and Hillrighaus, Ber. 24, 4182 (1891).

[11] E. Fischer, Ann. 232, 242 (1886).

[12] F. Bölsing and J. Tafel, Ber. 25, 1553 (1892).

[13] E. Fischer, Ann. 190, 174 (1878).

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SYNTHESIS OF ALIPHATIC AMINO ACIDS FROM THIOPHENE DERIVATIVES

I. SYNTHESIS OF α-AMINO ACIDS

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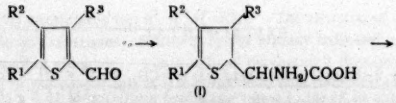
It is known that organic sulfur-containing compounds suffer hydrogenolysis under the influence of skeletal nickel catalyst, during which process sulfur is removed [1]. This method of sulfur elimination was used by a number of investigators to elucidate some of the questions relative to the structure of natural compounds, in particular of penicillin and biotin [2], and in some cases for synthesis purposes. The hydrogenolysis of thiophene derivatives is of especial interest, since, utilizing the aromatic properties of the thiophene ring, it is possible to introduce various substituents into it, and then by hydrogenolysis arrive at the desired aliphatic compounds. This method was used in our laboratory to obtain some difficultly available hydrocarbons, higher alcohols, glycols, acids, etc. [3]. This method was also used by other investigators to obtain certain aliphatic compounds (for example, [4]).

In this communication we present the data of our experiments on the preparation of some aliphatic amino acids from thiophene derivatives [5]. Having set ourselves this task, we outlined the following methods for its solution:

1) The introduction of both functional groups into the ring, for example, the carboxyl and nitro groups, and subsequent simultaneous reduction of the NO_2 group and cleavage of the thiophene ring with the aid of the mentioned catalyst.

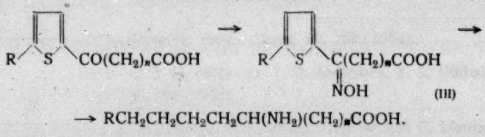
2) The synthesis of ulenylamino acids, containing both functional groups in the side chain, and their hydrogenolysis by the scheme:



$$\rightarrow R^1CH_2CH(R^2)CH(R^3)CH_2CH(NH_2)COOH.$$
(II)

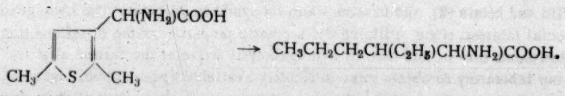
With this method it was possible to obtain α-amino acids with either a normal or a branched chain of carbon atoms. The second possibility is realized in the case where either R^2 or R^3 is an alkyl radical, or if the aldehyde group is found in the β-position of the thiophene ring.

3) The synthesis of hydroxyimino acids of the thiophene series from the corresponding ketocarboxylic acids with a variable number of methylene groups between the functional groups found in the side chain, and subsequent hydrogenolysis of the hydroxyimino acids:

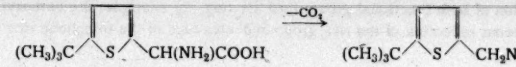


The realization of this scheme made it possible to obtain aliphatic amino acids with either a normal or a branched chain of C-atoms, and in addition, with a variable number of CH_2-groups between the HOOC- and NH_2-groups.

When we attempted to apply the first of the indicated methods to the case of 5-nitro-2-thiophenecarboxylic acid we succeeded in isolating only a very small amount of δ-aminovaleric acid; consequently, work in this direction was terminated. The second of the outlined methods proved to be fully acceptable, since in a number of cases the hydrogenolysis step proceeds with a yield of about 50%. In the experimental section we describe the preparation of three α-amino acids with a normal chain of carbon atoms (d,l-α-amino-n-caproic, d,l-α-amino-n-enanthic and d,l-α-amino-n-caprylic acids) and one α-amino acid with an isostructure, namely d,l-α-amino-β-ethylcaproic acid from d,l-α-amino-(2,5-dimethyl-3-thienyl) acetic acid:



The hydrogenolysis of d,l-α-amino-(5-tert-butyl-2-thienyl)-acetic acid did not give the desired d,l-α-amino-ζ,ζ-dimethyl-caprylic acid in a pure state. Of interest is the fact that in the synthesis of d,l-α-amino-(5-tert-butyl-2-thienyl)-acetic acid from 5-tert-butyl-2-thiophenecarboxaldedyde we isolated, together with the amino acid, 5-tert-butyl-2-thienylamine, probably formed due to decarboxylation of the amino acid:



The third of the outlined methods also led to success. By this method we obtained α-amino-n-caproic acid from the oxime of 2-thienylglyoxylic acid, which proved to be identical with the hydrogenolysis product of α-amino-(2-thienyl) acetic acid.

EXPERIMENTAL

d,l-α-Amino-(5-methyl-2-thienyl) acetic acid [(I) R^1=CH_3, R^2, R^3 = H]. To a solution of 17.2 g (0.26 mole) of potassium cyanide in 30 ml of water was added a solution of 15.5 g (0.29 mole) of ammonium chloride in 40 ml of water. To this mixture was added a solution of 32.9 g (0.26 mole) of 5-methyl-2-thiophenecarboxaldehyde in 130 ml of methyl alcohol and 40 ml of concentrated ammonia solution. Here a yellow precipitate was formed. The reaction mass was shaken for 4 hours at 25°; a dark oil deposited toward the end of shaking. The mixture was poured into 500 ml of water and extracted with benzene. The benzene layer was washed with water and then with dilute (1:1) hydrochloric acid; the hydrochloric acid extracts were combined. The benzene layer after extraction with hydrochloric acid was washed with water, then with sodium bicarbonate solution, again with water, and dried over fused magnesium sulfate. After distilling off the benzene the residue was distilled at 4.5 mm; here 2.2 g of unreacted 5-methyl-2-thiophenecarboxaldehyde with b. p. 69-70° and n_D^{20} 1.5805 was obtained. The residue in the flask was 5.3 g of a dark and extremely viscous tar. The hydrochloric acid extract (see the procedure used above) was heated under reflux for four hours. From the obtained solution a small amount of 5-methyl-2-thiophenecarboxaldehyde, was vacuum distilled, together with water. The residue (about 250 ml) was then heated with activated charcoal, the charcoal was removed by filtration, and the filtrate evaporated to dryness in vacuo. The mixture obtained here of d, l-α-amino(5-methyl-

2-thienyl)acetic acid and ammonium chloride was dried in a vacuum-desiccator over calcium chloride and potassium hydroxide; the weight of the mixture was 36.6 g. This mixture was dissolved in 300 ml of water, the solution was filtered, and the filtrate was treated with an excess of saturated copper acetate solution. The resulting coppersalt precipitate was washed several times with water and dried over phosphoric anhydride. Weight of the salt 24.3 g (49.2%). To obtain the free amino acid a stirred suspension of the finely divided copper salt in 1000 ml of water was treated for 2 hours with a stream of hydrogen sulfide. Activated charcoal was added to the mixture, the solution was heated to the boil and filtered, and the filtrate was evaporated to dryness in vacuo (bath temperature of about 60°). The residue weighed 17.32 g (the yield of crude amino acid was 41.5%, based on reacted aldehyde). The crude amino acid was recrystallized from dilute (1 : 1) alcohol. The yield of purified amino acid with m. p. 199-200° (decomp.) * was 10.5 g. The melting point of the amino acid strongly depends on the rate of heating the apparatus.

Found %: C 49.03, 49.10; H 5.41, 5.60; S 18.38, 18.54. $C_7H_9O_2NS$. Calculated %: C 49.10; H 5.30; S 18.73.

The hydrochloride of d,l-α-amino (5-methyl-2-thienyl) acetic acid melts at 182-183°.

Found %: Cl 17.42, 17.50. $C_7H_9O_2NS \cdot HCl$. Calculated %: Cl 17.55.

The p-toluene-sulfonyl derivative of the amino acid, after recrystallization from dilute alcohol melts at 176-177° (with decomp.).

Found %: N 4.53, 4.46. $C_{14}H_{15}O_4NS_2$. Calculated %: N 4.31.

d,l-α-Amino (5-ethyl-2-thienyl) acetic acid [(I) $R^1 = C_2H_5$, R^2, R^3 = H]. The reaction of ammonium cyanide with 28.3 g of 5-ethyl-2-thiophenecarboxaldehyde and subsequent treatment gave 14.2 g of the copper salt (37.5%, based on reacted aldehyde). The weight of the recovered aldehyde was 3.7 g. We were unable to obtain the free amino acid when a stream of hydrogen sulfide was passed into a suspension of the amino acid copper salt in water, apparently due to the exceedingly low solubility of the copper salt in water. In this connection we had to resort to concentrated ammonia solution to make the salt soluble. Saturation of the solution obtained in this manner with hydrogen sulfide gave 9.95 g of crude amino acid. The latter was purified by recrystallization from dilute alcohol. The yield of amino acid with m. p. 213 (with decomp.) was 8.45 g. It should be mentioned that the melting point strongly depends on the rate of heating.

Found %: C 51.63, 51.84; H 6.02, 6.16; N 7.33, 7.51; S 17.45, 17.38. $C_8H_{11}O_2NS$. Calculated %: C 51.87; H 5.99; N 7.56; S 17.31.

The p-toluene-sulfonyl derivative of the amino acid, after recrystallization from dilute alcohol, melts at 172-173°.

Found %: N 4.13, 4.17. $C_{15}H_{17}O_4NS_2$. Calculated %: N 4.13.

d,l-α-Amino (2-thienyl) acetic acid [(I) R^1, R^2, R^3 = H]. The reaction of ammonium cyanide with 28.8 g of 2-thiophenecarboxaldehyde and subsequent treatment by the already indicated method gave 12 g of the dry copper salt (28%, based on reacted aldehyde). The weight of unreacted 2-thiophenecarboxaldehyde was 3.5 g (n_D^{20} 1.5871). Decomposition of the copper salt of the amino acid with hydrogen sulfide gave 8.25 g of impure amino acid; after repeated recrystallization from water it melted at 223-224° (with decomp.). The melting point strongly depends on the rate of heating. The amino acid gives a blue-violet coloration with ninhydrin.

Found %: C 45.92, 46.05; H 4.65, 4.53; N 8.75, 8.66; S 20.19, 20.07. $C_6H_7O_2NS$. Calculated %: C 45.84; H 4.49; N 8.91; S 20.40.

The p-toluene-sulfonyl derivative after recrystallization from dilute alcohol with rapid heating melted at 159-160°.

Found %: N 4.74, 4.73. $C_{13}H_{13}O_4NS_2$. Calculated %: N 4.50.

d,l-α-Amino (2-thienyl) acetic acid was obtained earlier [6] in poor yield by the reduction of 2-thienylglyoxylic acid oxime with tin and hydrochloric acid. The amino acid, obtained by us from 2-thiophenecarboxaldehyde through the corresponding aminonitrile, did not depress the melting point when mixed with the amino acid obtained by the reduction of 2-thienylglyoxylic acid oxime. Their p-toluenesulfonyl derivative also did not show a mixed melting point depression (159-160° with decomp.).

* In all cases the melting points of the amino acids were determined in a sealed capillary in a previously heated apparatus.

d,l-α-Amino (2,5-dimethyl-3-thienyl)acetic Acid was synthesized by the above described method from 2,5-dimethyl-3-thiophenecarboxaldehyde, which in turn was obtained from the 2,5-dimethylthiophene fraction isolated from shale gasoline. To identify the 2,5-dimethylthiophene the 2,5-dimethylacetothienone was prepared from this fraction, the oxime of which melted at 81.5-82° and which did not depress the melting point when mixed with the 2,5-dimethyl-3-acetothienone oxime obtained from synthetic 2,5-dimethylthiophene (a melting point of 83° is given in the literature [7] for this oxime).

To a solution of 13.0 g of 2,5-dimethyl-3-thiophenecarboxaldehyde (n_D^{20} 1.5636) in 75 ml of methyl alcohol was added a solution of 6.6 g of potassium cyanide and 6 g of ammonium chloride in 35 ml of water, and then 50 ml of concentrated ammonia solution. The mixture was shaken for 7 hours at room temperature; here an orange oil deposited toward the end of reaction. The mixture was poured into 500 ml of water and then extracted with benzene, after which the benzene layer was shaken 3 times with dilute (1:1) hydrochloric acid. The hydrochloric acid extract was boiled for 3 hours under reflux; here a tar deposited. The solution was diluted with 500 ml of water, separated from the tar, and after heating with activated charcoal, was evaporated in vacuo. The dry residue (a mixture of amino acid hydrochloride and ammonium chloride) weighed 16.0 g. The residue was dissolved in 100 ml of water, the solution was filtered from some turbidity and then neutralized (to Congo) by the addition of ammonia, and then with an excess of saturated sodium acetate solution. The precipitate of amino acid was filtered, washed with water, and dried. Weight 6.86 g, m. p. 182-185° (with decomp.). The yield of impure amino acid was about 40%. We were unable to isolate the unreacted 2,5-dimethyl-3-thiophenecarboxaldehyde. Recrystallization from water gave 4.58 g of d,l-α-amino (2,5-dimethyl-3-thienyl) acetic acid with m. p. 203-204° (with decomp.).

Found %: C 51.74, 51.55; H 6.16, 6.00; N 7.29, 7.35; S 17.24, 17.38. $C_8H_{11}O_2NS$. Calculated %: C 51.87; H 5.99; N 7.56; S 17.31.

The p-toluenesulfonyl derivative of the amino acid, after recrystallization from dilute alcohol, melted at 172-173° (with decomp.).

Found %: N 4.17, 4.25. $C_{15}H_{17}O_4NS_2$. Calculated %: N 4.13.

d,l-α-Amino (5-tert-butyl-2-thienyl) acetic acid was synthesized by the above described method from 5-tert-butyl-2-thiophenecarboxaldehyde; the 2-tert-butylthiophene was obtained by the reaction of isobutylene with thiophene [8] in the presence of 75% H_2SO_4. The thiosemicarbazone of the aldehyde melted at 194° (with previous softening). A m. p. of 197° is given in the literature [9] for this thiosemicarbazone.

Found %: N 17.45, 17.38. $C_{10}H_{15}N_3S_2$. Calculated %: N 17.42.

We obtained 13.04 g (29%) of crude amino acid from 35.8 g of the aldehyde. After recrystallization from water the amino acid melted at 186-187° (with decomp.).

Found %: C 56.22, 56.02; H 7.02, 7.12; S 15.02, 15.09. $C_{10}H_{15}O_2NS$. Calculated %: C 56.30; H 7.09; S 15.04.

The p-toluenesulfonyl derivative of the obtained amino acid, after recrystallization from dilute alcohol, melted at 159.5-160.5°.

Found %: N 3.77, 3.87. $C_{17}H_{21}O_4NS_2$. Calculated %: N 3.81.

A colorless oil was obtained when alkali was added to the mother liquor from the recrystallization of the amino acid. The oil was extracted with ether, the extract was dried over potassium hydroxide, and the ether was distilled off. When dissolved in hydrochloric acid the residue gave 1.4 g of 5-tert.-butyl-2-thienylamine hydrochloride; after recrystallization from water the hydrochloride melted at 229-230°.

Found %: C 52.67, 52.82; H 7.90, 7.78; N 6.96, 6.94. $C_9H_{16}NClS$. Calculated %: C 52.70; H 7.83; N 6.81.

The addition of picric acid to a solution of the hydrochloride gave the picrate of 5-tert.-butyl-2-thienylamine with m. p. 185-186° (from water).

Found %: N 14.07, 13.81. $C_{15}H_{18}O_7N_4S$. Calculated %: N 14.06.

The nitranilate of this amine is very difficultly soluble in hot water, practically insoluble in alcohol and ethyl acetate, and decomposes without melting.

Hydrogenolysis of d,l-α-amino (5-methyl-2-thienyl) acetic acid – preparation of d,l-α-amino-n-enanthic acid [(II) $R^1 = CH_3$, R^2, $R^3 = H$]. Two grams of d,l-α-amino (5-methyl-2-thienyl) acetic acid with m. p. 200° was dissolved with heating in a solution of 0.7 g of sodium carbonate in 100 ml of distilled water. To the cooled solution was added about 9 g of skeletal nickel catalyst. The mixture was boiled under reflux with good stirring for 1 hours. The catalyst after cooling was filtered and repeatedly washed with hot distilled water. The combined filtrates were evaporated in vacuo to a volume of about 50 ml. The solution was acidified with dilute acetic acid. The precipitate of α-amino-n-enanthic acid was filtered, washed with dilute alcohol, and dried in a vacuum desiccator over P_2O_5. Weight 0.76 g. The addition of copper acetate solution to the mother liquor gave about 0.16 g of the copper salt of α-amino-n-enanthic acid. As a result, the total yield of α-amino-n-enanthic acid was 0.90 g (53%). The amino acid was purified by recrystallization from water. M. p. 279-280° (with decomp.). A m. p. of 281° is given in the literature [10].

Found %: C 57.91, 57.95; H 10.29, 10.42; N 9.33, 9.39. $C_7H_{15}O_2N$. Calculated %: C 57.90; H 10.41; N 9.65.

After recrystallization from dilute alcohol the benzoyl derivative of α-amino-n-enanthic acid (obtained by the method described in [11]) melted at 133-134°; a m. p. of 135° is given for it in the literature [12].

Found %: N 5.81, 5.65. $C_{14}H_{19}O_3N$. Calculated %: N 5.62.

Hydrogenolysis of d,l-α-amino (5-ethyl-2-thienyl) acetic acid – preparation of d,l-α-amino-n-caprylic acid [(II) $R^1 = C_2H_5$, R^2, $R^3 = H$]. Treatment of 3.00 g of d,l-α-amino(5-ethyl-2-thienyl) acetic acid under conditions similar to those described above gave after acidification 0.98 g of crude d,l-α-amino-n-caprylic acid and 0.1 g of its copper salt. As a result, the total yield of the amino acid was 1.06 g (41%). The amino acid was purified by recrystallization from water. M. p. 270-271° (with decomp.). A m. p. of 270° is given for this amino acid in the literature [10].

Found %: C 60.24, 60.15; H 10.73, 10.81; N 8.67, 8.75. $C_8H_{17}O_2N$. Calculated %: C 60.34; H 10.76; N 8.80.

After recrystallization from dilute alcohol the benzoyl derivative of the obtained amino acid melted at 125-126°. In the literature [10] a m. p. of 128° is given for the benzoyl derivative of d,l-α-amino-n-caprylic acid.

Found %: C 68.31, 68.17; H 8.10, 8.01; N 5.05, 5.14. $C_{15}H_{21}O_3N$. Calculated %: C 68.42; H 8.04; N 5.32.

Hydrogenolysis of d,l-α-amino (2-thienyl) acetic acid – preparation of d,l-α-amino-n-caproic acid (Norleucine). [(II) R^1, R^2, $R^3 = H$]. The hydrogenolysis was run the same as for d,l-α-amino (5-methyl-2-thienyl) acetic acid. From 2.3 g of d,l-α-amino (2-thienyl) acetic acid we obtained 0.32 g of crude d,l-α-amino-n-caproic acid and 1.00 g of its copper salt. The total yield of amino acid was 1.13 g (59%). The amino acid was purified by recrystallization from water. M. p. 275-277° (with decomp.). For this amino acid various authors give a melting point ranging from 273-327° (for example [12-14]).

Found %: C 54.35, 54.51; H 9.90, 10.00; N 10.38, 10.47. $C_6H_{13}O_2N$. Calculated %: C 54.94; H 9.99; N 10.68.

After recrystallization from dilute alcohol the benzoyl derivative had m.p. 132°; m.p. 134° [11].
Found %: N 5.90, 5.91. $C_{13}H_{17}O_3N$. Calculated %: N 5.96.

Hydrogenolysis of α-thienylglyoxylic acid oxime [(III) n = 0] – preparation of d,l-α-amino-n-caproic acid. To a solution of 3 g of α-thienylglyoxylic acid oxime (for the preparation of this ketoacid and its oxime [5]) in 50 ml of water was added 1.3 g of soda and 20 ml of concentrated ammonia solution (the ammonia addition increases the yield during the hydrogenolysis of the oxime). The reaction mass was stirred with 15 g of skeletal nickel catalyst at 70-75° until the qualitative test for sulfur was negative (test with sodium nitroprusside). About 2 hours was required to complete the hydrogenolysis. After filtering to remove catalyst and neutralizing with acetic acid to remove aluminum hydroxide the solution was treated with a solution of copper acetate. The precipitate of the amino acid copper salt was 1.31 g (50%). Decomposition of the copper salt with hydrogen sulfide gave 0.59 g of free amino acid, which after recrystallization from water melted at 273-274° (with decomp).

Found %: N 10.30, 10.37. $C_8H_{13}O_2N$. Calculated %: N 10.68.

After recrystallization from dilute alcohol the benzoyl derivative of the obtained amino acid melted at 132° and did not depress the melting point when mixed with the benzoyl derivative of the d,l-α-amino-n-caproic acid obtained by the hydrogenolysis of d,l-α-amino (2-thienyl) acetic acid (see above).

Found %: C 66.20, 66.16; H 7.25, 7.21; N 5.72, 5.68. $C_{13}H_{17}O_3N$. Calculated %: C 66.32; H 7.28; N 5.96.

Hydrogenolysis of d,l-α-amino (2,5-dimethyl-3-thienyl) acetic acid – preparation of d,l-α-amino-β-ethylcaproic acid. To a solution of 3.7 g of d,l-α-amino (2,5-dimethyl-3-thienyl) acetic acid and 2.3 g of soda in 75 ml of water and 20 ml of concentrated ammonia solution at 70° was added with stirring about 15 g skeletal nickel catalyst. The reaction mass was stirred at 70-75° for 1 hour until the qualitative test for sulfur was negative. After filtering off the catalyst and acidifying with dilute acetic acid the solution was treated with copper acetate to give 1.95 g of the copper salt of the acid (51%). Decomposition of the copper salt with hydrogen sulfide gave 1.26 g of the free amino acid, which after recrystallization from water, and then from methanol, had m. p. 244-246° (with decomp.).

Found %: C 60.17, 60.21; H 10.32, 10.20; N 8.74, 8.88. $C_8H_{17}O_2N$. Calculated %: C 60.34; H 10.76; N 8.80.

The p-toluenesulfonyl derivative of the amino acid, after recrystallization from dilute alcohol, had m.p. 105.5-107°.

Found %: N 4.50, 4.49. $C_{15}H_{23}O_4NS$. Calculated %: N 4.47.

SUMMARY

1. The reaction of ammonium cyanide with 2-thiophenecarboxaldehydes and subsequent hydrolysis of the resulting aminonitriles gave five α-amino acids of the thiophene series: α-amino (5-ethyl-2-thienyi)-acetic acid, α-amino (2-thienyl) acetic acid, α- amino (2,5-dimethyl-3-thienyl) acetic acid α- amino (5-tert.-butyl-2-thienyl) acetic acid and α-amino (5-methyl-2-thienyl) acetic acid.

2. The hydrogenolysis of four of the synthesized amino acids of the thiophene series with skeletal nickel catalyst gave α-amino acids of the aliphatic series: α-amino-n-enanthic acid, α-amino-n-caprylic acid, α-amino-n-caproic acid and α-amino-β-ethylcaproic acid.

3. The hydrogenolysis of α-thienylglyoxylic acid oxime gave α-amino-n-caproic acid.

LITERATURE CITED

[1] J. Bougault, E. Cattelain and P. Chabrier, Bull. soc. chim. France, [6] 34 (1939); [7] 780 (1940).

[2] S. Harris, R. Mozingo, D. Wolf, A. Wilson and K. Folkers, J. Am. Chem. Soc. 67, 2102 (1945).

[3] Ya. L. Goldfarb and M. S. Kondakova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 1131; Ya. L. Goldfarb and I. S. Korsakova, Proc. Acad. Sci. USSR 96, 283 (1954); Ya. L. Goldfarb and M. L. Kirmalova, J. Gen. Chem. 25, 1373 (1955) (T. p. 1321).*

[4] F. F. Blicke and D. G. Sheets, J. Am. Chem. Soc. 71, 4010 (1949); D. Papa, E. Schwenk and H. Ginsberg, J. Org. Chem. 14, 723 (1949).

[5] Ya. L. Goldfarb and B. P. Fabrichny, Proc. Acad. Sci. USSR 100, 461 (1955).

[6] W. P. Bradley, Ber. 19, 2122 (1886).

[7] F. Zilberfarb, J. Russ. Phys.-Chem. Soc. 45, 1938 (1914).

[8] Caesar, J. Am. Chem. Soc. 70, 3623 (1948); H. D. Hartough, Thiophene and its Derivatives (New York, 1952), 497.

*T. p. = C. B. Translation pagination.

[9] M. Sy, N. P. Buu-Hoi and N. Dat. Xuong, J. Chem. Soc. 1954, 1975.

[10] N. F. Albertson, J. Am. Chem. Soc. 68, 450 (1946).

[11] E. Fischer, Ber. 33, 2382 (1900).

[12] H. Kudielka, Monatsh. 29, 353 (1908).

[13] M. S. Dunn and T. W. Brophy, J. Biol. Chem. 99, 221 (1932).

[14] A. Darapsky, J. prakt. Chem. 146, 219 (1936).

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CATALYTIC AMINATION OF ORGANIC COMPOUNDS

IV. AMINATION OF BUTYL ALCOHOLS

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As is known, the catalytic amination of alcohols was first studied in 1909 by Sabatier and Mailhe [1]. As catalysts they investigated various dehydration oxides – those of aluminum, thorium, zirconium, etc.

Popov [2, 3] investigated 11 different catalysts for this reaction, of which the most active proved to be activated carbon, platinum-on-carbon and platinized silica gel; however, the yield of amination products was always small. Thus, in the case of using platinum on silica gel at 400° there was obtained 13 g of catalyzate from 20 g of n-butyl alcohol, which catalyzate contained 48.07% amines. Popov noticed that the greatest yield of amines is obtained when the primary butyl alcohol is aminated, a considerably smaller yield when the secondary alcohol is aminated, while the tertiary alcohol yields only a very small amount of amines. In the work of Heinemann and others [4] the amination of n-butyl alcohol was made over bauxite at 320°. Here it was observed that the presence of iron oxide as impurity noticeably activates the catalyst. In a number of patents [5] it is indicated that the use of aluminum oxide together with dehydrogenation catalysts – nickel, cobalt, chromium, and also with either molybdenum or vanadium oxide, favors the formation of substantial amounts of butyronitrile. But the introduction of hydrogen into the reaction mass reduces the formation of the nitrile and favors the formation of butylamines. In the work of Davies and others [6, 7] the amination of n-butyl alcohol was run over copper catalyst in a hydrogen atmosphere at a pressure of 10-15 atm.

The purpose of the present investigation was to study the catalytic amination of the butyl alcohols of different structure with compressed ammonia using a commercial activated aluminum oxide. The alcohols aminated were n-butyl alcohol, isobutyl alcohol and trimethylcarbinol. The reaction and working up of the reaction products were done the same as described earlier [8]. The method of Mizuch and Savchenko [9] was used to analyze the amination products.

In this investigation we studied the influence of the ammonia pressure, temperature, contact time of the reactants with the catalyst surface, and the chemical structure of the butyl alcohols on the yield of amines. The results obtained by us on the catalytic amination of the butyl alcohols are presented in the Table.

From the data given in the Table it can be concluded that the ammonia pressure exerts a strong influence on both the reaction course and the yield of final reaction product. Thus, in the amination of n-butyl alcohol with ammonia at atmospheric pressure the yield of amines is extremely slight, but at the same time a large amount of butylene is liberated (determined by the bromate-bromide method [10]).

With increase in the ammonia pressure in the reaction zone the yield of amines shows substantial increase, and that of butylene shows strong decrease, i. e., the dehydration reaction of the butyl alcohol is suppressed, and the amination reaction becomes predominant. This fact deserves interest from both the theoretical and practical viewpoints.

At 250° the yield of amines is extremely small, and it reaches its maximum at 350-380°. With further elevation of the temperature the yield of amines drops sharply, and at the same time the amount of gaseous products shows a strong increase. Without doubt both the alcohol and the formed amines are decomposed at elevated temperature.

Expt. Nos.	Name of alcohol	Amount of alcohol (in g)	NH_3 pressure (in atm.)	Experimental temperature	Number of drops (per minute)	Yield of amines (in % on reacted alcohol)	Composition of amines (in %)			Amount of gas (in liters)
							primary	secondary	tertiary	
1	n-Butyl	40.0	1	370—380°	20	17.3	58.2	30.5	11.3	8.0
2	The same	24.0	3	370—380	20	41.1	59.2	30.2	10.5	6.0
3	" "	40.0	7	370—380	20	58.8	59.1	25.2	15.7	3.5
4	" "	40.0	9	370—380	20	69.3	57.0	27.5	15.5	2.5
5	" "	40.0	10	370—380	20	87.6	—	—	—	1.5
6	" "	24.0	9	370—380	10	89.9	62.0	29.8	8.2	4.5
7	" "	40.0	9	370—380	45	58.1	48.1	40.8	11.1	2.5
8	" "	24.0	9	250	20	37.4	—	—	—	0.5
9	" "	24.0	9	400	20	18.8	50.4	28.6	21.0	6.0
10	Isobutyl	40.0	9	370—380	20	52.1	59.6	26.1	14.3	5.5
11	The same	40.0	9	370—380	10	68.8	51.4	40.7	7.7	4.0
12	" "	40.0	9	400	20	26.4	59.6	26.4	14.0	12.0
13	Trimethylcarbinol	20	9	370—380	20	25.3	—	—	—	—

The greatest amount of amines is formed when primary alcohols are aminated. A tertiary alcohol gives a small yield of amines, but by using compressed ammonia we obtained a higher yield of amines than did Popov in the experiments run at atmospheric pressure. As a result, in the catalytic amination of alcohols with compressed ammonia it is possible to obtain a mixture of primary, secondary and tertiary amines in good yield, with a predominance of the primary amines. The individual amines can be isolated from these mixtures by fractional distillation. Thus, the amination of 82 g of n-butyl alcohol gave 40 g of mixed amines, the fractional distillation of which gave 24 g of monobutylamine with b. p. 76-77°, d_4^{20} 0.743, n_D^{20} 1.412, picrate m. p. 151°, and 12 g of dibutylamine with b. p. 159-161°, d_4^{20} 0.766, n_D^{20} 1.423, which is in accord with the literature data [11]. The fractional distillation of 32 g of mixed amines, obtained in the amination of 60 g of isobutyl alcohol, gave 18 g of isobutylamine with b. p. 66-67°, d_4^{20} 0.7359, n_D^{20} 1.397, and 8 g of diisobutylamine with b. p. 140-141°, d_4^{20} 0.746, n_D^{20} 1.405, which also is in accord with the literature data [11].

SUMMARY

1. The catalytic amination of n-butyl, isobutyl and tertiary butyl alcohols with compressed ammonia over aluminum oxide was studied.

2. It was established that by using compressed ammonia it is possible to suppress dehydration of the alcohols, and for the case of primary alcohols the amination reaction becomes the main reaction, which assures a high yield of amines (up to 90%, based on reacted alcohol).

LITERATURE CITED

[1] P. Sabatier, Catalysis in Organic Chemistry (1932), p. 181.

[2] A. M. Popov, J. Gen. Chem. 18, 438 (1948).

[3] A. M. Popov, J. Gen. Chem. 18, 1109 (1948).

[4] Heinemann, et al., Ind. Eng. Chem. 41, 2928 (1949).

[5] U. S. Patent Nos. 2365727 (1944), 2349222 (1944), 2487299 (1949), 2389500 (1945), 2394515 and 2394516 (1946).

[6] U. S. Patent No. 2609394 (1950).

[7] Swiss Patent No. 292409 (1953).

[8] N. Kozlov and N. Panova, J. Gen. Chem. 25, 183 (1955).(T. p. 167).*

[9] Org. Chem. Ind. 7, 24 (1940).

[10] A. N. Blazhenova et al., Analysis of Gases in the Chemical Industry (State Chem. Press, 1954), p. 205.

[11] Dictionary of Organic Compounds (1949), I, 358, 727; Chemist's Handbook (State Chem. Press, 1951), II, 354, 400.

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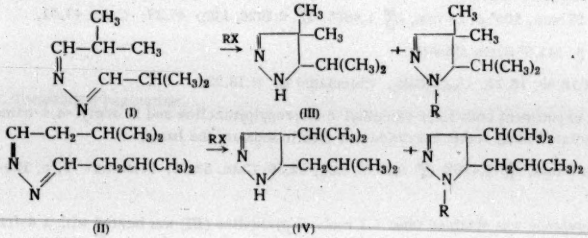
*T. p. = C. B. Translation pagination.

REACTION OF HYDRAZINE DERIVATIVES

VIII. CYCLIZATION OF ALDAZINES UNDER THE INFLUENCE OF ALKYL HALIDES

A. N. Kost, I. I. Grandberg and G. A. Golubeva

The transformation of acetone azine into N-alkyl-3,5,5-trimethylpyrazolines under the influence of alkyl halides was described in a previous communication [1]. In the present study it was shown that the azines of isobutyraldehyde (I) and isovaleraldehyde (II) under the influence of alkyl halides behave in a similar manner, giving respectively 4,4-dimethyl-5-isopropylpyrazoline (III) and 4-isopropyl-5-isobutylpyrazoline (IV), together with their N-alkyl derivatives.



It had been mentioned earlier that in pyrazoline bases a noticeable molecular association effect is observed due to the presence of the NH-group [2]. Actually, in the alkylation of pyrazolines the boiling point of the substance fails to rise for the lower alkyls, and even drops somewhat, which makes it difficult to separate the mixed bases. Acylation with acetic anhydride was not always a satisfactory separation method, since this reagent at times caused strong tarring. If the mixture is benzoylated by the Schotten-Baumann method, then the N-alkyl-pyrazolines are easily isolated. A change in the polarity of the pyrazoline molecules after their alkylation sharply influences the molecular refraction (a sizeable increment appears).

From the data obtained by us we assumed a value of 6.245 for the group refraction of the two nitrogen atoms (together with the double bond) in N-alkylpyrazolines, instead of the value 5.871, determined earlier for pyrazolines with a free NH-group [3].

EXPERIMENTAL

Reaction of isobutyraldehyde azine (I) with allyl bromide. A mixture of 35 g (~ 0.25 mole) of azine (I) [3] with 60.5 g (0.5 mole) of allyl bromide was heated to the boil and cooled after 1 hour. After separating 2.8 g of the pyrazoline (III) hydrobromide crystals (m. p. 153°, with decomp.) the liquid mass was dissolved in 300 ml of acidified water and extracted twice with dichloroethane. The aqueous layer was made alkaline, extracted with ether, the extract dried over magnesium sulfate, and then distilled. We obtained 13 g of pyrazoline (III)

(b. p. 107-117° for 50 mm, n_D^{20} 1.4627, oxalate, m. p. 109° [1]) and 11 g of a fraction with b. p. 108-128° at 20 mm, the fractional distillation of which gave 5.1 g (11.3%) of 1-allyl-4,4-dimethyl-5-isopropylpyrazoline:

B. p. 108-114° at 9-10 mm, n_D^{20} 1.4742, d_4^{20} 0.8933, MR_D 56.74. Calc. 56.58. Found %: N 15.23, 15.40. $C_{11}H_{20}N_2$. Calculated %: 15.55.

Reaction of azine (I) with benzyl chloride. To 28 g (0.2 mole) of azine (I) was added 25.2 g (0.2 mole) of benzyl chloride. The greater portion of the mixture crystallized after 24 hours. Six grams of 4,4-dimethyl-5-isopropylpyrazoline (III) hydrochloride was isolated; m. p. 148° (literature, m. p. 143° [1], 149° [2]). The residual liquid was hydrolyzed by boiling for 3 hours with 150 ml of 2N hydrochloric acid to decompose unreacted azine, then it was made strongly alkaline, extracted with ether, the extracts dried over potash, and distilled. Here another 3.8 g of pyrazoline (III) was obtained as the free base (total yield 38%), b. p. 90-94° at 40 mm, n_D^{20} 1.4596. From the heavy fraction after 2 distillations we isolated 15 g (32%) of 1-benzyl-4,4-dimethyl-5-isopropylpyrazoline:

B. p. 114° at 9 mm, n_D^{20} 1.5140, d_4^{20} 0.9557, MR_D 72.56; Calc. 71.92.

Picrate, m. p. 145° (from alcohol).

Found %: N 15.10, 15.21. $C_{21}H_{24}O_7N_5$. Calculated %: N 15.21.

Reaction of azine (I) with methyl iodide. A mixture of 70 g (~ 0.5 mole) of azine (I) and 113 g (~ 0.8 mole) of methyl iodide was boiled for 5 hours. Here salt deposition failed to be observed. After treatment similar to that described above the mixture of bases was benzoylated by the Schotten-Baumann method, extracted with ether, and distilled. The amount of 1,4,4-trimethyl-5-isopropylpyrazoline isolated was 18.9 g (26.4 %):

B. p. 95° at 27 mm, 100° at 29 mm, n_D^{20} 1.4605, d_4^{20} 0.8926, MR_D 47.37; Calc. 47.81.

Picrate, m. p. 141.5° (from alcohol).

Found %: N 18.09, 18.17. $C_{15}H_{21}O_7N_5$. Calculated %: N 18.23.

In a similar experiment both 1,4,4-trimethyl-5-isopropylpyrazoline and N-acetyl-4,4-trimethyl-5-isopropylpyrazoline were isolated when acetic anhydride was used to separate the bases:

B. p. 113° at 9 mm, n_D^{20} 1.4762, d_4^{20} 0.9712, MR_D 52.90; Calc. 53.28. Literature b. p. 120-125° at 13 mm [4].

The same substance was obtained when 0.1 mole of pyrazoline (III) was heated with a 4-fold amount of acetic anhydride on the water bath for 4 hours. Yield 71%, b. p. 127° at 18 mm, n_D^{20} 1.4766.

Reaction of isovaleraldehyde azine (II) with methyl iodide. A mixture of 42 g (~ 0.25 mole) of azine (II) [3] and 71 g (0.5 mole) of methyl iodide was boiled for 2.5 hours. After the usual treatment we isolated 28 g of a fraction with b. p. 105-108° at 12-14 mm. After benzoylation and distillation we obtained 10.2 g (22.7%) of 1-methyl-4-isopropyl-5-isobutylpyrazoline:

B. p. 113° at 26 mm, n_D^{20} 1.4542, d_4^{20} 0.8755, MR_D 56.41; Calc. 56.05. Found %: C 72.59, 72.66; H 12.26, 12.29. $C_{11}H_{22}N_2$. Calculated %: C 72.47; H 12.16.

Picrate, m. p. 116° (from alcohol).

Found %: N 16.83, 16.85. $C_{17}H_{25}O_7N_5$. Calculated %: N 16.96.

Reaction of acetone azine with ethyl iodide. A mixture of 56 g (0.5 mole) of acetone azine and 140.5 g (0.9 mole) of ethyl iodide was boiled for 10 hours. After the usual treatment, with benzoylation, we obtained 17.4 g (24.2%) of 3,5,5-trimethyl-1-ethylpyrazoline:

B. p. 64° at 30 mm, n_D^{20} 1.4512, d_4^{20} 0.8713, MR_D 43.34; Calc. 43.19.

Picrate, m. p. 92° (from alcohol).

Found %: N 18.08, 18.16. $C_{14}H_{19}O_7N_5$. Calculated %: N 18.28.

If acetic anhydride is used for the separation, then considerable tarring is observed. We were able to isolate in the pure state only 1-acetyl-3,5,5-trimethylpyrazoline with b. p. 82-84° at 5 mm. The same substance was

also obtained by boiling 3,5,5-trimethylpyrazoline with excess acetic anhydride for 4 hours. Yield 71%, b. p. 80.5° at 4 mm; m. p. 42-42.5°.

Found %: C 62.19, 62.39; H 9.08, 9.13. $C_9H_{14}ON_2$. Calculated %: C 62.30; H 9.15.

SUMMARY

When reacted with alkyl halides the azines of isobutyraldehyde and isovaleraldehyde are converted into the corresponding 4,5-dialkylpyrazolines and their N-alkyl derivatives.

LITERATURE CITED

[1] A. N. Kost, G. A. Golubeva and I. I. Grandberg, J. Gen. Chem. 26, 1976 (1956) (T. p. 2201).*

[2] H. Hayes and L. Hunter, J. Chem. Soc. 1941, 1.

[3] A. N. Kost and I. I. Grandberg, J. Gen. Chem. 26, 2319 (1956).

[4] A. Franke, Monatsh. 20, 864 (1899).

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STUDY OF THE SULFONATION REACTION

XL. QUANTITATIVE DETERMINATION OF BENZENEDISULFONIC ACIDS

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In industry benzene is sulfonated to the m-disulfonic acid for the production of resorcinol, which is obtained in low yield. The disulfonation of benzene cannot be considered a well studied process, which is chiefly explained by the absence of convenient and sufficiently accurate methods of determining the individual isomers in sulfonation mixtures. Thus, Holleman and Polak [1] determined the amount of m- and p-benzenedisulfonic acids formed during sulfonation from the fusion diagram of the m- and p-disulfonyl chlorides. This method cannot be used if the ortho-isomer is present in the mixture, and also if mono- or trisulfonic acids are present. Behrend and Mertelsmann [2] divided the crystallization of the m- and p-benzenedisulfonic acid sodium salts into 3-5 fractions. Each fraction was converted into the dichlorides, which crystallized from ligroin in various forms. Then the crystals were separated by direct selection. In addition to being extremely cumbersome, the method is only suitable in the absence of acids other than the meta- and para-isomers.

Quite a few methods are described in the literature for the determination of various sulfonic acids as their arylamine salts [3].

In the present study we also used the different solubility of some arylamine salts of the benzenedisulfonic acids for the quantitative determination of the ortho-, meta- and para-isomers. The method is applicable in the presence of the benzenemono- and trisulfonic acids.

EXPERIMENTAL

The foundation for developing the method was a study of the solubilities of the salts of 18 amines with the o-, m- and p-disulfonic acids, the mono- and the trisulfonic acids of benzene. The tests were made as follows. To 10 ml of a water solution of the amine hydrochloride was slowly added from a burette a 0.7% solution of the sulfonic acid sodium salt until a precipitate appeared. The experimental results, presented in Table 1, permit assigning a semiquantitative value to the solubility of a number of sulfonic acid arylamine salts in water with an excess of the amine hydrochloride present in solution. The precipitate of the sulfonic acid amine salt appeared after the addition of the indicated amount (in milliliters) of sodium sulfonate solution. The readily soluble salts fail to give a precipitate even after the addition of a substantial amount of the sodium salt solution, which fact is also noted in the Table. Of the investigated amines the most suitable for the quantitative determination of the isomers proved to be the first three: phenylhydrazine, benzidine and 2-naphthylamine.

Directions for determining the o-disulfonic acid as the phenylhydrazine salt. A sample of about 5 g of the sulfonation mixture was dissolved in a 100 ml flask. Aliquots (25 ml) of the solution were neutralized with 0.5 N alkali solution in the presence of phenolphthalein, then 40 ml of warm 1 N phenylhydrazine hydrochloride solution was added, the solution made up to a volume of 75 ml, and placed in ice. After 2 hours the precipitate was separated on a small funnel, the flask rinsed with the filtrate, and the precipitate washed 5-6 times with 1 ml portions of ice water until it tested negative for chloride ion, thoroughly suction-filtering each time. The precipitate with filter were rinsed into a flask to a volume of about 150 ml and titrated at the boil with 0.1 N alkali solution, using phenolphthalein as indicator.

TABLE 1

Appearance of a Precipitate After the Indicated Volume of Sodium Sulfonate Solution Had Been Added to 10 ml of the Amine Hydrochloride Solution

Hydrochloride solution	Normality	0.7% Solutions of the isomeric sodium benzenedisulfonates (in ml)			3% Sodium sulfate solution (in ml)
		ortho-	meta-	para-	
Phenylhydrazine	0.5	0.03	12 no ppt.	12 no ppt.	15 no ppt.
Benzidine	0.2	0.06	12 no ppt.	0.1	0.03
2-Naphthylamine	0.2	0.03	12 no ppt.	0.03	0.03
p-Anisidine	0.5	14 no ppt.	12 no ppt.	12 no ppt.	3
o-Anisidine	0.5	14 no ppt.	12 no ppt.	12 no ppt.	4
Dianisidine	0.2	0.9	12 no ppt.	12 no ppt.	5 no ppt.
o-Tolidine	0.5	0.03	12 no ppt.	1	
1-Naphthylamine	0.2	12 no ppt.	12 no ppt.	0.7	0.03
Aniline	0.5	12 no ppt.	12 no ppt.	12 no ppt.	
o-Toluidine	0.5	12 no ppt.	12 no ppt.	12 no ppt.	0.2
m-Toluidine	0.5	12 no ppt.	12 no ppt.	12 no ppt.	
m-4-Xylidine	0.5	8	12 no ppt.	12 no ppt.	
Pseudocumidine	0.5	0.9	3.5	0.5	
Benzylisothiourea	0.5	0.03	12 no ppt.	0.5	
p-Aminoacetophenone	0.5	7	12 no ppt.	12 no ppt.	
m-Nitro-o-anisidine	0.18	3.7	12 no ppt.	12 no ppt.	2.5
p-Nitro-o-toluidine	0.084	3	12 no ppt.	12 no ppt.	2.5
m-Nitroaniline	0.5	0.25	12 no ppt.	3.5	

Remarks: All of the amine solutions given in the Table fail to give a precipitate with 12 ml of a 0.7% solution of benzenemono- and -trisulfonic acids.

To determine the sum of sulfonic acids and sulfuric acid a 5 ml aliquot of the solution was titrated with 0.1 N alkali solution, the solution acidified with hydrochloric acid, and the sulfuric acid determined gravimetrically as barium sulfate.

The results of testing the method on artificially prepared mixtures, presented in Table 2, show that the error in determining the ortho-isomer fails to exceed 2.3%, while the average error is 1.1%. Since the obtained result is always lower than the true value, the introduction of a constant correction factor of 1.1% makes the maximum error 1.2%.

Determination of the sum of the o- and p-disulfonic acids as the 2-naphthylamine salts. The procedure was exactly the same as that described above, except that about a 1 g sample of the sulfonation mixture is taken, and 50 ml of 0.2 N 2-naphthylamine hydrochloride solution is used for the precipitation. The total volume of the solution prior to putting in ice is made up to 100 ml. Since here the o- and p-disulfonic acids are precipitated together with sulfuric acid, it becomes necessary to subtract the amount of sulfuric acid from the obtained result.

The sum of the disulfonic acids and sulfuric acid is also determined by titrating 25 ml of the solution with 0.1 N alkali, and subsequent gravimetric determination of the sulfuric acid in the acidified solution.

The amount in percent of the sum of o- and p-disulfonic acids in the sulfonation mixture is calculated by the formula:

$$\frac{1.191}{S} \cdot \frac{V_k}{V_p} (a - 85.68 \cdot z) = \% \text{ ortho- and para-isomers,}$$

TABLE 2

Determination of o-Benzenedisulfonic Acid in Artificially Prepared Mixtures

Taken					Found o-benzenedisulfonic acid (in %)	Error (in %)
isomeric disulfonic acids (in % of their total)			disulfonic acids (in g)	sulfuric acid (in g)		
ortho-	meta-	para-				
34.5	65.5		0.3282	0.4256	32.4	—2.1
42.7		57.3	0.2322	0.3570	42.3	—0.4
27.7	50.0	22.3	0.4637	0.4350	26.6	—1.1
64.2	20.6	15.2	0.6018	0.9891	61.9	—2.3
42.6	45.3	12.1	0.5120	0.5552	42.1	—0.5
14.5	62.8	22.7	0.5522	0.4958	14.4	—0.1

TABLE 3

Determination of the Sum of o- and p-Benzenedisulfonic Acids in Artificially Prepared Mixtures

Taken					Found		Error in determining the ortho- and para-isomers (in %)
isomeric disulfonic acids (in % of their sum)			disulfonic acids (in g)	sulfuric acid (in g)	o- and p-disulfonic acid (in %)	sulfuric acid (in g)	
ortho-	para-	meta-					
55.1	21.7	23.2	0.2562	0.0430	76.8		0
12.0	24.0	64.0	0.2069	0.1008	35.9		—0.1
41.9	13.1	45.0	0.1224	0.1399	53.6		—1.4
39.4	8.9	51.7	0.1085	0.1389	48.3		0
40.2	12.5	47.3	0.1012	0.1561	52.3	0.1561	—0.4
10.6	19.9	69.6	0.1951	0.0956	30.2	0.0942	—0.3

where: S is the weight of the sulfonation mixture, v_k and v_p are the volumes of the flask and pipette, respectively, a is the number of milliliters of 0.1 N alkali consumed in titrating the arylamine salts, and z is the weight of barium sulfate (in grams).

The total amount of disulfonic acids is calculated by the same formula, only instead of "a" the number of milliliters of 0.1 N alkali, consumed in titrating the total acidity, is substituted.

The results of testing the method on artificially prepared mixtures, presented in Table 3, show that the error of determining the sum of the ortho- and para-isomers fails to exceed 1.4% of the sum of the disulfonic acids.

Directions for determining the p-disulfonic acid as the benzidine salt in the absence of the ortho-isomer. When the ortho-isomer is absent in the mixture, which apparently is frequently encountered in sulfonation mixtures, the para-isomer can be determined in the following manner. A sample of the mixture, weighing about 5 g, is dissolved in a 100 ml flask. Then a 25 ml aliquot of the solution is taken, heated to the boil, and neutralized with hot saturated barium hydroxide solution in the presence of phenolphthalein. The excess barium hydroxide is removed with 0.5 N sulfuric acid solution, the volume of the solution is made up to 50 ml by the mark on the flask, and with boiling is added 50 ml of 0.2 N benzidine hydrochloride solution. After standing for 10-15 minutes the solution is placed on ice for 2 hours, then the precipitate is removed, washed 4-5 times with ice water (in 5 ml portions) until the test for chloride ion is negative, the precipitate together with filter rinsed into a flask, and then titrated at the boil with 0.1 N alkali in the presence of phenolphthalein.

These directions are not applicable in the presence of o-benzenedisulfonic acid, since the barium salt of the ortho-isomer is difficultly soluble and precipitates together with the barium sulfate.

The results of testing this procedure on artificially prepared mixtures, presented in Table 4, show that the determination error fails to exceed 0.7% of the sum of the disulfonic acids.

TABLE 4

Determination of p-Benzenedisulfonic Acid in Artificially Prepared Mixtures

Taken				Found p-benzene-disulfonic acid (in %)	Error (in %)
isomeric disulfonic acids (in % of their sum)		disulfonic acids (in g)	sulfuric acid (in g)		
para-	meta				
45.6	54.4	0.3707	—	45.0	—0.6
44.0	56.0	0.3163	0.380	43.6	—0.4
43.0	57.0	0.3874	0.410	42.5	—0.5
29.3	70.7	0.4542	0.498	29.6	+0.3
17.8	82.2	0.2933	0.325	18.5	+0.7
10.6	89.4	0.2127	0.416	10.5	—0.1

The amount of sulfuric acid can be determined by taking 5 ml of the investigated solution and precipitating the para-isomer and sulfuric acid with 2-naphthylamine by the preceding procedure, and then subtracting from the obtained result the amount of para-isomer found with the aid of benzidine. The total acidity is determined by titration. As a result, in the absence of the ortho-isomer the whole analysis is run volumetrically.

TABLE 5

Determination of Benzenedisulfonic Acids in Sulfonation Mixtures, Obtained by the Sulfonation of Benzene With the Addition of Pure Sulfonic Acids

Expt. No.	Sulfonic acids in the sulfonation mixture (in % of their sum)			Composition, calculated after adding the pure acids (in %)					Found (in % of the sum of sulfonic acids)			Error (in % of the sum of sulfonic acids)		
	ortho	para-	meta	ortho	para-	meta	mono-	tri-	ortho	para-	meta	ortho	para-	meta
1	0	3.9	96.1	10.5	15.0	69.3	3.0	2.2	10.7	15.5	69.9	0.2	0.5	0.6
2	0	3.9	96.1	9.3	19.0	62.3	5.9	3.5	8.9	18.3	63.3	0.4	0.7	1.0
3	0	4.6	95.4	0	28.9	58.8	6.7	5.6	—	28.3	59.4		0.6	0.6

The results of checking the method on sulfonation mixtures, obtained by the direct sulfonation of benzene, are presented in Table 5. The benzene was mixed in the cold with 60% oleum (4 parts), sulfonated for 8 hours at 170°, and the sulfonation mixture analyzed by the method given above. Then to a solution of the mixture were added pure o-, m- and p-disulfonic, and also mono- and trisulfonic acids, and the new mixture was analyzed for the amount of ortho-, meta- and para-isomers. In Expts. 1 and 2 (Table 5) the analysis was made through the phenylhydrazine and 2-naphthylamine salts. In the case of Expt. 3 a part of the sulfonation mixture from Expt. 1 was treated with 98% sulfuric acid, for the purpose of binding excess sulfuric anhydride, and the mixture was again heated at 228° for 8 hours. The sulfonation mixture was analyzed through the benzidine salts.

The results show that the method can be used in the presence of the mono- and trisulfonic acids of benzene, and is suitable for the analysis of sulfonation mixtures obtained by the direct sulfonation of benzene.

The amines used in the study were purified either by recrystallization from various solvents or by distillation.

The disulfonic acids were prepared by the saponification of the corresponding disulfonyl chlorides. The o-benzenedisulfonyl chloride with m. p. 142° was obtained by us from ortho-chloronitrobenzene; the m-benzenedisulfonyl chloride with m. p. 61° was obtained by the direct sulfonation of benzene, and the p-disulfonyl chloride with m. p. 139° was obtained from sulfanilic acid through 4,4'-diphenyl disulfide-disulfonic acid.

SUMMARY

Semiquantitative tests of the solubilities of the salts of 18 amines with o-, m- and p-disulfonic acids were made.

A volumetric method was proposed for determining the amount of o-benzenedisulfonic acid in sulfonation mixtures via its precipitation as the phenylhydrazine salt.

A volumetric method was proposed for determining the sum of the o- and p-benzenedisulfonic acids in mixtures through the 2-naphthylamine salts.

In the absence of the ortho-isomer the para-isomer is determined by its precipitation as the benzidine salt.

The error in determining the isomers does not exceed 0.7-1.4% of the sum of the disulfonic acids.

The determination can be run in the presence of the mono- and trisulfonic acids of benzene.

LITERATURE CITED

[1] A. F. Holleman and J. J. Polak, Rec. trav. chim. 29, 416 (1910).

[2] R. Behrend and M. Mertelsmann, Ann. 378, 352 (1911).

[3] A. A. Chuksanova and I. M. Bilik, Aniline Dye Ind. 3, 459 (1933); Z. E. Zinkov et al., J. Appl. Chem. (USSR) 9, 1997 (1936); A. A. Spryskov and B. I. Karavaev, J. Gen. Chem. 22, 1620 (1952) (T. p. 1663). *

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SYNTHESIS OF SUBSTITUTED BENZYLAMINES AND N-BENZYL-β-CHLOROPROPIONAMIDES

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Very recently the attention of pharmacologists has been drawn to N-benzyl-β-chloropropionamide, which under the name of "Hibicon" finds use as an anticonvulsant [1, 2]. In searching for active compounds with a similar action the synthesis of a considerable number of N-acyl derivatives of benzylamine had been accomplished, which differed from each other in the nature of the acid group, in which number were included both substituted and unsubstituted carboxylic acids and sulfonic acids [3].

Together with this, any information relative to the influence of substituents in the aromatic ring of the benzylamine on the anticonvulsant activity is absent.

For the purpose of elucidating this question we synthesized several compounds of this type, having substituents in the aromatic ring of the benzyl radical; we selected the β-chloropropionyl radical as the acylating group, thus assuring maximum pharmacological effect. The substituted N-benzyl-β-chloropropionamides were synthesized by the scheme:

$$ArCH_2Cl \rightarrow ArCH_2NH_2 \rightarrow ArCH_2NHCOCH_2CH_2Cl.$$

The p-methylbenzyl-, p-methoxybenzyl-, 3,4-dimethoxybenzyl- and p-nitrobenzylamides of β-chloropropionic acid were obtained for the first time. In addition, we synthesized the earlier described [3] p-chlorobenzamide. For the purpose of elucidating the influence of replacing the benzyl nucleus by another aromatic radical we prepared N-(α-naphthyl)-methyl-β-chloropropionamide by the same scheme.

Various methods are described in the literature for the synthesis of the individual substituted benzylamines needed by us, most of which are associated with starting materials that are relatively difficult to obtain. We obtained all of the substituted benzylamines by one method – replacement of the chlorine atom in the corresponding benzyl chlorides by the amino group through the urotropine salts:

$$ArCH_2Cl + C_6H_{12}N_4 \rightarrow ArCH_2Cl \cdot C_6H_{12}N_4 \rightarrow ArCH_2NH_2.$$

Apparently, up to now this method has been used only for obtaining benzylamine itself, and its expansion for the synthesis of nuclear-substituted benzylamines is described by us for the first time. Its chief advantage over the existing methods for the synthesis of compounds of this type reduces to its simplicity and availability of the starting substituted benzyl chlorides, easily obtained by the chloromethylation of aromatic compounds. The most convenient operating technique proved to be the following: benzyl chloride (or a substituted benzyl chloride) is treated with urotropine in either chloroform or dichloroethane solution at 40-60° for several hours; after being kept at room temperature for 15-20 hours the urotropine complex (yield 90-95%) is filtered, washed with chloroform, dried, and then decomposed under slight warming with a mixture of concentrated hydrochloric acid and methanol. The amine is isolated from the obtained solution in the usual manner. For further purification it is most convenient to isolate the amine as the free base; only in the case of the p-chlorobenzyl- and p-nitrobenzylamines did we prefer to work with the hydrochloride, due to the difficulties that arose in purifying the free base.

In the preparation of the p-methoxy- and 3,4-dimethoxybenzylamines, in connection with the large losses incurred in isolating the corresponding methoxy-substituted benzyl chlorides in the pure state, for the preparation of the urotropine complexes we preferred to use directly the solutions of these compounds in dichloroethane, which solutions were obtained in the chloromethylation.

We obtained benzylamine in about 75% yield; the yields of the nuclear-substituted benzylamines were 40-60%. All of the substituted benzylamines that we prepared, and also the α-naphthylmethylamine, are colorless, viscous, oily liquids, avidly attracting carbon dioxide from the atmosphere. Consequently, to obtain the pure compounds it is necessary to take suitable precautions.

Then the obtained benzylamines and α-naphthylmethylamine were acylated with β-chloropropionyl chloride. The reaction was run in water medium [3], with simultaneous addition of the chloride and sodium hydroxide. For successful synthesis the pH of the reaction mixture should be in the limits 8.0-8.5. If the amine hydrochloride is used in the synthesis, then its water solution is previously neutralized with sodium hydroxide. Only in the case of obtaining the N-p-nitrobenzyl-β-chloropropionamide were we forced to use a different method. In this case the acylation was run in chloroform solution, without the addition of alkali; here half of the amine tied up the liberated hydrogen chloride, precipitating as the hydrochloride; the obtained amide was isolated by evaporation of the chloroform solution.

The substituted N-benzyl-β-chloropropionamides, obtained in yields of 50 to 80%, and also the N-(α-naphthyl)-methyl-β-chloropropionamide, are colorless, completely stable, crystalline substances, difficultly soluble in water, and soluble in organic solvents. They were tested for their anticonvulsant action.*

The greatest antispasmodic action, equal to that of "Hibicon" [3], was shown by N-(3,4-dimethoxybenzyl)-β-chloropropionamide. A somewhat weaker anticonvulsant action was shown by N-(p-chlorobenzyl)-β-chloropropionamide. N-(p-methoxybenzyl)-β-chloropropionamide not only failed to show anticonvulsant action, but even raised the convulsion of rabbits. The remaining benzamides proved to be inactive.

EXPERIMENTAL

I. Preparation of Benzylamines

1. Benzylamine. To a solution of 121 g of urotropine in 700 ml of chloroform was gradually added with stirring 87 g of freshly distilled benzyl chloride. The mixture was stirred at 60-70° for 4 hours and then let stand for 18 hours at room temperature. The obtained precipitate of urotropine salt was filtered, washed with chloroform, and air-dried (190.5 g; yield 91%). The salt was decomposed by heating it for a short time in 800 ml of a concentrated hydrochloric acid-methanol mixture (1:3); the precipitate of ammonium chloride was filtered, the mother liquor was evaporated in the vacuum of a water-jet pump to a volume of 300-350 ml, an excess of a concentrated aqueous solution of sodium hydroxide was added, the amine was extracted with ether, the extract was dried over either potash or caustic, and the solvent was removed by distillation. Distillation of the residue gave 55.6 g (76%) of benzylamine with the following constants:

B. p. 73-75° at 12 mm, n_D^{20} 1.5410, d_4^{20} 0.9826, MR_D 34.24; Calculated 34.34.
Literature: b. p. 184-185° [4]; n_D^{20} 1.5401, d_4^{20} 0.9797 [5].

2. p-Methylbenzylamine. Obtained in the same manner as the previous from 53 g of urotropine and 53 g of p-methylbenzyl chloride in 400 ml of chloroform. Isolation and decomposition of the urotropine salt gave 20.4 g (45.6%) of p-methylbenzylamine with the following constants:

B. p. 84-85° at 10 mm, n_D^{20} 1.5375, d_4^{20} 0.9666, MR_D 39.18; Calculated 38.96.

The substance is a colorless liquid, avidly attracting carbon dioxide from the atmosphere.

Literature: b. p. 195° [6]; n_D^{20} 1.5364, d_4^{20} 0.9520 [7].

*The tests were run by N. V. Kaverin under the supervision of Prof. V. S. Zakusov.

3. α-Naphthylmethylamine. Obtained in a similar manner from 69.5 g of α-chloromethylnaphthalene and 55 g of urotropine in 400 ml of chloroform. After standing for 2 hours the urotropine salt was separated and worked up the same as described above; we obtained 27.2 g (44 %) of α-naphthylmethylamine with the following constants:

B. p. 153-155° at 12 mm, n_D^{20} 1.6405, d_4^{20} 1.0958, MR_D 51.32; Calculated 49.68.
Literature: b. p. 155° at 12 mm [8].

The substance is a viscous colorless liquid, avidly attracting carbon dioxide from the atmosphere.

4. p-Methoxybenzylamine. Into a suspension of 72.5 g of anisole and 22.2 g of paraform in 300 ml of dry dichloroethane with stirring was passed for 3 hours a stream of dry hydrogen chloride at 15-20°; the mixture was let stand overnight, then washed with 300 ml of water, the dichloroethane solution dried over fused potash, and then used to obtain the urotropine salt without isolating the p-methoxybenzyl chloride. The obtained solution was gradually added with stirring to a suspension of 92 g of urotropine in 200 ml of dry dichloroethane; the mixture was heated for some time at 35-45° and allowed to stand for 16 hours. The urotropine salt was isolated and decomposed with 950 ml of a concentrated hydrochloric acid-methanol mixture, the same as described above. The obtained solution of the amine hydrochloride was evaporated in vacuo until all of the methylal had been removed, water was added to dissolve the partially precipitated amine hydrochloride, and after treatment with alkali and the usual isolation technique we obtained 32 g (35.7 %, based on anisole) of p-methoxybenzylamine with the following constants:

B. p. 110-113° at 11 mm, n_D^{20} 1.5452, d_4^{20} 1.0583, MR_D 41.19; Calculated 40.61.
Found %: N 10.55. $C_8H_{11}ON$. Calculated %: N 10.22.
Literature [9]: b. p. 236-237°, d^{15} 1.050.

The substance is a colorless oily liquid with characteristic odor, eagerly absorbing carbon dioxide from the atmosphere.

The picrate was obtained in aqueous alcohol; light-yellow needles with m. p. 184-185° (from aqueous alcohol).

Found %: N 15.17; 14.93. $C_{14}H_{14}O_8N_4$. Calculated %: N 15.29.
Literature: m. p. 188° [10].

5. 3,4-Dimethoxybenzylamine. Obtained in the same manner as before from 108 g of veratrole and 23.8 g of paraform in 400 ml of dry dichloroethane in a stream of dry hydrogen chloride. The solution of the chloromethylation product was converted into the urotropine salt by treatment with 78.8 g of urotropine; the urotropine salt was isolated and decomposed as described above; the amine was extracted with a mixture of ether and ethyl acetate (2:1); after drying and distillation we obtained 42 g (32%, based on veratrole) of 3,4-dimethoxybenzylamine with the following constants:

B. p. 155-156° at 16 mm, n_D^{20} 1.5520, d_4^{20} 1.1224, MR_D 47.27; Calculated 46.89.
Found %: N 8.35, 8.43. $C_9H_{13}O_2N$. Calculated %: N 8.38.
Literature [11]: b. p. 154-158° at 12 mm, d^0 1.1430.

The substance is a heavy colorless liquid, eagerly absorbing carbon dioxide from the air.

The picrate was obtained in alcohol. Fine yellow prisms with m. p. 174-175° (from alcohol).

Found %: N 13.70. $C_{15}H_{16}O_9N_4$. Calculated %: N 14.10.
Literature [11]: m. p. 169°.

6. p-Nitrobenzylamine. The urotropine salt (89 g, yield 90%) was obtained from 54.0 g of p-nitrobenzyl chloride and 45 g of urotropine in 500 ml of chloroform; the salt was decomposed with 400 ml of a concentrated hydrochloric acid-methanol mixture under short heating at 50-60°; after removing the ammonium chloride the mother liquor was condensed in vacuo and the obtained p-nitrobenzylamine hydrochloride was removed by filtration; yield 38.7 g (66%). Glistening light-yellow crystals with m. p. 235-240°.

Found %: Cl 18.69, 18.83. Calculated %: Cl 18.80.
Literature: m. p. 250° [12]. 224° [13].

The picrate was obtained in alcohol. Coarse light-yellow crystals with m. p. 184-185° (from alcohol).

Found %: N 18.33, 18.31. $C_{13}H_{11}O_9N_5$. Calculated %: N 18.37.
Literature [14]: m. p. 194°.

7. p-Chlorobenzylamine. Obtained in a similar manner from 25.0 g of p-chlorobenzyl chloride and 22 g of urotropine in 200 ml of chloroform (without heating), with subsequent decomposition of the salt (42.7 g, 91.3%) by the above-described method. The amine was isolated as the hydrochloride. Yield 16.7 g (60.7%), m. p. 248-250°.

Found %: Cl 19.70, 19.72. $C_7H_9NCl_2$. Calculated %: Cl 19.91.
Literature: m. p. 259° [15], 239-241° [16].

II. Preparation of N-Benzyl-β-Chloropropionamides

N-(3,4-Dimethoxybenzyl)-β-chloropropionamide. To 12 g of 3,4-dimethoxybenzylamine in 60 ml of water with vigorous stirring and cooling was simultaneously added in drops 9.13 g of β-chloropropionyl chloride and 2.86 g of sodium hydroxide in 15 ml of water, at a reaction temperature not exceeding 8-10°. On conclusion of stirring the reactants, the pH of the mixture was brought to 8.0-8.5 by the addition of a small amount of alkali, and the mixture was stirred for 30-40 minutes at room temperature. The precipitate of the amide was filtered, washed with cold water, and dried in a desiccator. Yield 11.5 g (62%). Tiny slender colorless needles with m. p. 113-114° (from alcohol), difficultly soluble in water, and soluble in organic solvents.

Found %: N 5.43, 5.53; Cl 13.56, 13.84. $C_{12}H_{16}O_3NCl$. Calculated %: N 5.44; Cl 13.76.

N-(p-Methoxybenzyl)-β-chloropropionamide. Obtained in a similar manner from 10.8 g of p-methoxybenzylamine (in 50 ml of water), 10.8 g of β-chloropropionyl chloride and 3.1 g of sodium hydroxide. Yield 11.6 g (65%). Slender colorless needles with m. p. 118-119° (from alcohol).

Found %: N 6.11, 6.13; Cl 15.60, 15.58. $C_{11}H_{14}O_2NCl$. Calculated %: N 6.12; Cl 15.58.

N-(p-Methylbenzyl) - β-chloropropionamide. Obtained in a similar manner from 8 g of p-methoxybenzylamine, 2.7 g of sodium hydroxide and 8.2 g of β-chloropropionyl chloride; yield 10.8 g (77%); colorless crystals, m. p. 98-99° (from alcohol).

Found %: N 6.66, 6.80; Cl 16.90, 16.98. $C_{11}H_{14}OClN$. Calculated %: N 6.61; Cl 16.75.

N-(α-Naphthyl)-methyl-β-chloropropionamide. Obtained in a similar manner from 8.4 g of α-naphthylmethylamine, 6.8 g of β-chloropropionyl chloride and 2.2 g of sodium hydroxide at 3-5°. Yield 10.2 g (51.2%); lustrous colorless crystals, m. p. 121-122° (from alcohol).

Found %: N 5.47; Cl 14.46, 14.29. $C_{14}H_{14}ONCl$. Calculated %: N 5.67; Cl 14.37.

N-(p-Chlorobenzyl)-β-chloropropionamide. To a warm solution of 8.0 g of p-chlorobenzylamine hydrochloride in 50 ml of water was added 1.8 g of sodium hydroxide in water in such a manner that the pH of the mixture was 8.0-9.0. The mixture was cooled to 7-10°, and at this temperature was simultaneously added 5.7 g of β-chloropropionyl chloride and 1.8 g of sodium hydroxide in water. Further treatment was by the above-described method. Yield 5.5 g (53%); fine lustrous needles, m. p. 124.5-125.5° (from alcohol).

Found %: N 6.47, 6.56; Cl 19.72, 19.70. $C_{10}H_{11}ONCl_2$. Calculated %: N 6.03; Cl 19.91.
Literature [3]: m. p. 125-126°.

N-(p-Nitrobenzyl)-β-chloropropionamide. Aqueous sodium hydroxide solution was added to 13.7 g of p-nitrobenzylamine hydrochloride, the resulting light-yellow oil was extracted with chloroform, and the extract was thoroughly dried over potash. To the dried extract with vigorous stirring and cooling to 2-3° was slowly added 7.0 g of β-chloropropionyl chloride, after which the mixture was stirred another 30 minutes. After a day the

fine precipitate of p-nitrobenzylamine hydrochloride was filtered, the mother liquor was evaporated in vacuo to dryness, the residue was dissolved in alcohol, the solution was poured into water, and the amide, separating as an oil, soon crystallized. An additional amount of the substance was obtained by a similar treatment of the filtered amine hydrochloride, since the amide is not too soluble in chloroform. Total 5.2 g (62.7 %). Pale-yellow crystals with m. p. 93-95° (from alcohol).

Found %: N 11.49, 11.69; Cl 14.48, 14.46. $C_{10}H_{11}O_3N_2Cl$. Calculated %: N 11.54; Cl 14.61.

SUMMARY

1. A general method was developed for the synthesis of substituted benzylamines from the corresponding benzyl chlorides through the urotropine salts.

2. A number of previously unknown substituted N-benzyl-β-chloropropionamides were prepared, which were tested for anticonvulsant action.

LITERATURE CITED

[1] M. Quevauviller and S. Garcet, Ann. pharm. franc. 11, 745 (1953).

[2] C. Hawkes, Arch. Neurol. Psychiat. 67, 815 (1952).

[3] S. Kushner, et al., J. Org. Chem. 16, 1283 (1951).

[4] W. Perkin, J. Chem. Soc. 69, 1208 (1896).

[5] M. Konovalov, Ber. 28, 1861 (1895).

[6] E. Bamberger and W. Lodter, Ber. 20, 1710 (1887).

[7] M. I. Konovalov, J. Russ. Phys.-Chem. Soc. 31, 254 (1898).

[8] J. Brau and G. Blissing, Ber. 56, 1996 (1923).

[9] M. Fiffeneau, Bull. soc. chim. 9, 819 (1911).

[10] C. K. Ingold and C. Shoppee, J. Chem. Soc. 1929, 1203.

[11] R. Douetteau, Bull. soc. chim. 9, 937 (1911).

[12] H. Ing and R. Manske, J. Chem. Soc. 1926, 2349.

[13] C. K. Ingold and E. Holmes, J. Chem. Soc. 1925, 1812.

[14] C. Wachendorff, Ann. 185, 266 (1877).

[15] Th. Curtius, J. prakt. Chem. (2), 89, 508 (1914).

[16] C. L. Jackson and A. W. Field, J. Am. Chem. Soc. 2, 95 (1880).

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ANTHRAQUINONES

XXVI. THE HYDROLYSIS OF ANTHRAQUINONE-1,5-DISULFONIC ACID*

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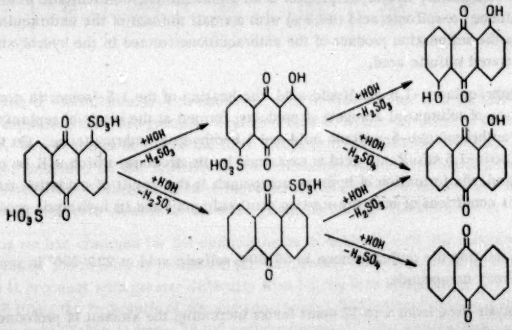
The conditions studied by us for the hydrolysis of anthraquinone-1,8-disulfonic acid [7] were transferred to the 1,5-disulfonic acid. The experiments on the hydrolysis of both the free anthraquinone-1,5-disulfonic acid and its sodium salt were run in sealed tubes with 0.0025 gram-mole of substance and 25 ml of either sulfuric acid or water.

In contrast to the anthraquinone-1,8-disulfonic acid and the anthraquinone-α-sulfonic acid, the behavior of the 1,5-disulfonic acid is characterized by a diversity of transformations, both in sulfuric acid [2] and in water [3].

The similar reactivity of both sulfo groups, and the similar influence exerted on each of them by the two carbonyl groups, does not permit obtaining a well-defined hydrolysis reaction. The hydrolysis of the anthraquinone-1,5-disulfonic acid in sulfuric acid (from 0.1 to 80%), in the absence of mercury salts, leads to replacement of either one or both sulfo groups by both hydrogen and hydroxyl groups. The hydrolysis of anthraquinone-1,5-disulfonic acid in water gave all of the theoretically possible hydrolytic transformation substances, formed in accord with the scheme:



The experiments on the hydrolysis of the anthraquinone-1,5-disulfonic acid show that the replacement of one of the sulfo groups in this sulfonic acid by either hydrogen or hydroxyl proceeds at a somewhat slower rate than is the case for the anthraquinone-α-sulfonic acid, but at a faster rate than for the anthraquinone-1,8-disulfonic acid. This is in agreement with the relative value of the velocity constants for the reaction of replacing one sulfo group by either hydrogen or chlorine, which values were determined by Lauer [4]. The hydrolysis, run at comparatively low temperatures, indicates a certain passivity of the anthraquinone-1,5-disulfonic acid when compared with the behavior of the 1,8-isomer under the same conditions. However, elevation of the hydrolysis temperature (190-260°) sharply increases the mobility of both of the sulfo groups in the anthraquinone-1,5-disul-

*See J. Gen. Chem., 25, 1206 (1955) for Communication XXV.

fonic acid. To a known degree such behavior for the anthraquinone-1,5-disulfonic acid is found to be in accord with its preparation. In the sulfonation of anthraquinone in the presence of mercury to the monosulfonic acid an elevation of the temperature (160-180°) sharply directs the process toward disulfonation, in which connection the amount of anthraquinone-1,5-disulfonic acid in the sulfonation mass is always greater than the amount of the 1,8-isomer. The hydrolysis of anthraquinone-1,5-disulfonic acid in 80% sulfuric acid at 230° for 6 hours proceeds to the extent of 30% with the formation of transformation products of one sulfo group as anthraquinone-α-sulfonic acid (9.8%) and 1-hydroxyanthraquinone-5-sulfonic acid (20%). At 260° the hydrolysis percent is doubled (70.6%), with also the formation now of transformation products of both of the sulfo groups of the original disulfonic acid as anthraquinone (42%), dihydroxyanthraquinone (19.1%) and 1-hydroxyanthraquinone-5-sulfonic acid (9.5%). Such behavior is observed when medium concentrations of H_2SO_4 are used for the hydrolysis. Thus, if the substance is heated in 20% sulfuric acid at 230° for 6 hours the predominant products are those that are formed by replacing one sulfo group by a hydroxyl (1-hydroxyanthraquinone-5-sulfonic acid – 28%, dihydroxyanthraquinone – 0.7%, and anthraquinone – 0.2%), while at 260° the hydrolysis percent shows a three-fold increase, and together with the transformation products of one sulfo group (anthraquinone-α-sulfonic acid – 23.8%, 1-hydroxyanthraquinone-5-sulfonic acid – 35%) there are also formed substantial amounts of the transformation products of both sulfo groups (dihydroxyanthraquinone – 8.2%, and anthraquinone – 28.6%).

Hydrolysis in weak sulfuric acid (0.1%) at 230° for 6 hours leads to replacement of the sulfo groups by hydroxyl with a small yield of dihydroxyanthraquinone (3.3%) and traces of the 1-hydroxy-5-sulfonic acid. The amount of unchanged anthraquinone-1,5-disulfonic acid is 91%. Under the same conditions, but at 260°, the total amount of unchanged 1,5-disulfonic acid is now only 1.8%, while the remainder represent hydrolysis products, both with replacement of the sulfo groups by hydrogen (anthraquinone 44%, anthraquinone-α-sulfonic acid 20%), and by hydroxyl-(dihydroxyanthraquinone 16%, 1-hydroxyanthraquinone-5-sulfonic acid 18%). An increase in the amount of anthraquinone is the result of a more profound hydrolysis when the sulfuric acid concentration is increased. Simultaneously with this the amount of anthraquinone-α-sulfonic acid is reduced (Table 1).

Beginning with 30% sulfuric acid and higher the hydrolysis is accompanied by tarring due to the oxidative processes that develop at elevated temperature. On the average the total yield of hydrolysis products is 72%. When the heating is in 90% sulfuric acid the hydrolysis is strongly retarded, and a substantial amount of disulfonic acid remains unchanged. The solitary hydrolysis product is an anthraquinonemonosulfonic acid, corresponding to a mixture of the anthraquinone-α-sulfonic acid (40.3%) with a small amount of the anthraquinone-β-sulfonic acid (4.0%). The latter is the sulfonation product of the anthraquinone formed in the hydrolysis of the 1,5-disulfonic acid with concentrated sulfuric acid.

In contrast to the anthraquinone-1,8-disulfonic acid, the heating of the 1,5-isomer in concentrated sulfuric acid leads to the appearance of substantial amounts of products, formed as the result of replacing the sulfo groups by hydroxyl, as 1-hydroxyanthraquinone-5-sulfonic acid and 1,5-dihydroxyanthraquinone. On the one hand, such behavior for the anthraquinone-1,5-disulfonic acid is explained by its structure, which will be communicated on separately; on the other hand, the formation of hydroxy compounds is the result of oxidative transformations under the drastic hydrolysis conditions of both the starting disulfonic acid and its hydrolysis product, namely anthraquinone.

The experiments on heating the anthraquinone in 50-90% sulfuric acid at 230-290° in sealed tubes lead to substantial amounts of hydroxy compounds.

Increasing the hydrolysis time from 6 to 12 hours favors increasing the amount of profound hydrolysis products of anthraquinone and dihydroxyanthraquinone.

The hydrolysis of anthraquinone-1,5-disulfonic acid in water also leads to a mixture of products. In contrast to the hydrolysis of the 1,8-isomer, a variation in the time, amount of water (Table 2) and temperature fail to lead to a predominance of substances of well-defined structure in the reaction medium. Only at 230° and 6 hours of heating was the formation of 3.3% of dihydroxyanthraquinone established, with 96.5% of unchanged disulfonic acid. The heating of anthraquinone-1,5-disulfonic acid in water at 260° reduces the amount of unchanged disulfonic acid to 2.8%, with the formation of anthraquinone-α-sulfonic acid (36.4%), anthraquinone (28.6%), 1-hydroxyanthraquinone-5-sulfonic acid (21.0%) and dihydroxyanthraquinone (10.8%). Further elevation of the hydrolysis temperature (290°) substantially raises the amount of anthraquinone (65%) and dihydroxyanthraquinone (30%), with the disappearance of the anthraquinone-α-sulfonic acid and 1-hydroxyanthraquinone-5-sulfonic acid.

TABLE 1

Influence of Sulfuric Acid Concentration on the Hydrolysis of Anthraquinone-1,5-disulfonic Acid [0.925 g (0.0025 g-mole) Substance, 25 ml H_2SO_4, 6 hours, 260°]

Expt. Nos.	H_2SO_4 concentration (in %)	Obtained (in %)				
		recovered disulfonic acid	anthraquinone	α-sulfonic acid	hydroxyanthraquinones	Na salt of 1-hydroxy-5-sulfonic acid
1	Water	2.8	28.6	36.4	10.8	21.0
2	0.1	1.8	43.9	19.7	16.4	18.0
3	0.25	4.3	15.2	44.3	8.2	28.0
4	0.5	4.3	11.4	49.2	5.0	28.0
5	20.0	4.3	28.6	23.8	8.2	35.0
6	30.0	2.2	26.6	14.0	11.6	17.0
7	40.0	0.7	33.8	4.9	18.1	11.5
8	50.0	0.7	38.0	4.9	20.7	7.5
9	70.0	None	38.2	None	17.3	13.0
10	80.0	None	42.0	None	19.1	9.5
11	90.0	38.7	None	44.3 *	Traces	None

TABLE 2

Influence of Amount of Water on the Hydrolysis of Anthraquinone-1,5-disulfonic Acid [0.925 g (0.0025 g-mole) Substance, 6 hours, 260°]

Expt. Nos.	Amount of water		Obtained (in %)				
	ml	molar	recovered disulfonic acid	anthraquinone	α-sulfonic acid	hydroxyanthrquinone	Na salt of 1-hydroxy-5-sulfonic acid
1	10	222.4	61.7	None	4.9	1.64	30.0
2	15	333.6	1.4	42.0	16.4	21.6	18.0
3	25	556.0	2.8	28.6	36.4	10.8	21.0
4	40	889.6	17.0	6.7	13.0	5.0	58.0

The hydrolysis of anthraquinone-1,5-disulfonic acid in either water or weak sulfuric acid proceeds to a larger degree of replacing the sulfo group by hydrogen than by hydroxyl, which is different from the behavior of the 1,8-isomer. Replacement of one of the sulfo groups in anthraquinone-1,5-disulfonic acid by the hydroxy group has a smaller influence on the mobility of the remaining sulfo group than is observed in the hydrolysis of the 1,8-isomer. The latter circumstance also indicates the independent influence exerted by the carbonyl oxygens of the anthraquinone molecule on each of the sulfo groups in the 1,5-disulfonic acid.

The same as we had observed for the anthraquinone-α-sulfonic acid and anthraquinone-1,8-disulfonic acid, the hydrolysis of either the sodium or potassium salt completely fails to proceed in water, while in weak sulfuric acid (0.25-0.5%) it proceeds with greater difficulty than for the free disulfonic acid (Table 3). In 70% sulfuric acid at 260° and 6 hours the hydrolysis of the anthraquinone-1,5-disulfonic acid sodium salt proceeds more uniformly. If the free acid (Table 1) forms 38.0% anthraquinone, 17.3% dihydroxyanthraquinone and 13.0% 1-hydroxyanthraquinone-5-sulfonic acid, then the sodium salt of the 1,5-disulfonic acid under these conditions gives 12.0% anthraquinone and 87.0% 1-hydroxyanthraquinone-5-sulfonic acid.

The experiments on heating anthraquinone-1,5-disulfonic acid in any concentration of sulfuric acid with the addition of mercury sulfate show, the same as in analogous experiments with anthraquinone-1.8-disulfonic acid, that mercury salts favor replacement of the sulfo group by hydrogen. Here a greater yield of hydrolysis products is attained, with a greater involvement of the starting disulfonic acid in hydrolysis at different temperatures (Table 4) than is the case for hydrolysis without mercury and for the 1,8-isomer.

TABLE 3

Influence of Time on the Hydrolysis of Anthraquinone-1,5-disulfonic Acid Sodium Salt in 0.5% Sulfuric Acid [1.035 g (0.0025 g-mole) Substance, 25 ml H_2SO_4, 290°]

Expt. Nos.	Time (in hours)	Obtained (in %)				
		recovered disulfonic acid	anthraquinone	α-sulfonic acid	hydroxyanthraquinone	Na salt of 1-hydroxy-5-sulfonic acid
1	1	13.0	7.6	23.0	21.5	35.0
2	3	1.3	24.8	18.4	18.2	37.0
3	6	2.8	34.4	30.0	21.5	10.0

TABLE 4

Influence of Mercury in the Hydrolysis of Anthraquinone-1,5-disulfonic Acid [0.925 g (0.0025 g-mole) Substance, 25 ml H_2SO_4, 6 hours]

Expt. Nos.	Temperature	H_2SO_4 concentration (in %)	Percent $HgSO_4$ in the disulfonic acid	Obtained (in %)				
				recovered disulfonic acid	anthraquinone	α-sulfonic acid	hydroxyanthraquinone	Na salt of 1-hydroxy-5-sulfonic acid
1	230°	0.25	None	86.2	0.19	None	0.5	12.2
2	230	0.25	5	70.4	3.0	8.2	Her	18.0
3	260	50.0	None	0.7	38.0	4.92	20.7	7.5
4	260	50.0	5	Her	57.0	32.0	8.2	Her
5	190	80.0	None	90.0	Her	Her	Her	Her
6	190	80.0	5	37.4	36.3	8.2	Her	Her
7	230	80.0	None	48.8	Her	9.8	Her	Her
8	230	80.0	10	37.4	30.5	24.6	3.2	Traces

EXPERIMENTAL

For hydrolysis we took anthraquinone-1,5-disulfonic acid [5] with m. p. 310° (needles, found M 368.2; calculated M 369, dried at 140-150°). After reaction the contents of the tube, in which the hydrolysis was run, were poured into 50 ml of water. In nearly all cases the odor of SO_2 was detected. The hydrolyzate from heating in concentrated sulfuric acid was usually dark-colored. The obtained precipitate was filtered, washed on the filter with hot water, dried in a desiccator, and weighed. The precipitate gives a cherry-red color with sodium hydroxide solution. The precipitate was treated with 1 N sodium hydroxide solution, the insoluble portion was filtered, washed on the filter with hot water, dried, and weighed. By known criteria this portion was assumed to be anthraquinone. It can also be shown in the sublimate when the originally isolated precipitate is heated. In this case the hydroxyanthraquinones mixed with it either burn, or remain on the surface of the porcelain plate on which the precipitate is heated. Acidification of the alkaline solution gave a precipitate, which was filtered, washed with water, dried in a desiccator, and weighed. The obtained product was assumed to be a mixture of 1,5-dihydroxyanthraquinone and α-hydroxyanthraquinone (m. p. 212-215°). A part of the precipitate dissolved when this mixture was treated with alcohol. A substance was isolated from the alcohol, which after recrystallization, again from alcohol did not depress the melting point when mixed with pure α-hydroxyanthraquinone (193°). The alcohol-insoluble portion of the precipitate was recrystallized from acetic acid to give orange-yellow crystals with m. p. 278-279°. This substance did not depress the melting point when mixed with pure 1,-5-dihydroxyanthraquinone [6].

The original mother liquor from the hydrolysis reaction, freed from the mixed precipitate of anthraquinone and hydroxyanthraquinones, contains 1-hydroxyanthraquinone-5-sulfonic acid (shown by its color with sodium

hydroxide solution), anthraquinone-α-sulfonic acid and unreacted anthraquinone-1,5-disulfonic acid.

For the quantitative characterization of this mixture a small amount of hydrochloric acid was added to the solution and the mixture treated for 2 hours at 98° with potassium chlorate. In separate experiments it was established that the 1-hydroxy-5-sulfonic acid is completely decomposed under the influence of oxidative hydrolysis. The chlorate treatment gave a precipitate of chloroanthraquinone, most frequently being a mixture of α-chloro anthraquinone and 1,5-dichloroanthraquinone. The amount of each of the chloroanthraquinones in the mixture was determined from the melting points of artificial mixtures of the indicated chloroanthraquinones [7]. The amount of 1-hydroxyanthraquinone-5-sulfonic acid was determined by salting out the sodium salt of this acid from alkaline solution. This substance was obtained as needles when recrystallized from water.

Analysis of the sodium salt of 1-hydroxyanthraquinone-5-sulfonic acid:

5.20 mg dry substance (experiment 1, Table 1): 1.19 mg Na_2SO_4; 4.61 mg dry substance (experiment 4, Table 1): 1.03 mg Na_2SO_4. Found%: Na 7.41, 7.23. $C_{14}H_7O_7SNa$. Calculated %: Na 7.05.

SUMMARY

1. The hydrolysis of anthraquinone-1,5-disulfonic acid in either sulfuric acid or water is possible without participation of mercury salts, but at elevated temperature and in sealed tubes.

2. The hydrolysis proceeds with the formation of replacement products of both one and two sulfo groups by both hydrogen and hydroxyl. Hydrolysis in concentrated sulfuric acid is accompanied by oxidation-reduction reactions, which lower the yield of hydrolysis products and favor the appearance of hydroxyanthraquinone compounds.

3. Mercury salts lower the temperature conditions needed for hydrolysis, at the same time favoring replacement of the sulfo groups by hydrogen with greater involvement in hydrolysis of the original disulfonic acid.

4. The character of the hydrolysis permits establishing the fact that the two sulfo groups in anthraquinone-1,5-disulfonic show equal reactivity, which follows from the uniform influence exerted on them by the carbonyl oxygens.

LITERATURE CITED

[1] V. V. Kozlov, J. Gen. Chem. 25, 1206 (1955) (T. p. 1153).*

[2] V. V. Kozlov and A. A. Egorova, J. Gen. Chem. 25, 809, 997 (1955) (T. p. 963).*

[3] V. V. Kozlov, Proc. Acad. Sci. USSR 61, 281 (1948); V. V. Kozlov and N. A. Kozlova, Author's Certificate 72, 484 (1947-1948).

[4] K. Lauer, J. prakt. Chem. 135, 182 (1932).

[5] H. E. Fierz-David, Helv. Chim. Acta 10, 205 (1927).

[6] Beilst. 8, 453.

[7] H. Meyer, Analysis and Determination of Organic Compounds. (1937), p. 360.

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*T. p. = C. B. Translation pagination.

HALOGENATION OF AROMATIC SILANES

III. PREPARATION AND PROPERTIES OF SOME CHLORO- AND BROMO-DERIVATIVES OF BENZYLTRICHLOROSILANE

G. V. Motsarev and A. Ya. Yakubovich

We had already mentioned earlier [1] that the halogenation of phenylchlorosilanes in the presence of catalysts is a peculiar reaction, since the formation of the halophenylchlorosilanes is accompanied by secondary destructive halogenation reactions (cleavage at the C–Si bond), and the substitution itself in the ring proceeds in an anomalous manner – instead of meta- there is observed ortho-, para-orientation. In studying these reactions various bromo- [2] and chloro-derivatives of phenyltrichlorosilane [3] and chloro-derivatives of diphenyldichlorosilane [4] were obtained.

It seemed of interest to study the halogenation of various other aromatic silanes, for example, those containing in the aromatic ring either the same or different substituents, or those containing the $SiCl_3$ group in the hydrocarbon side chain. Below we describe the results of halogenating benzyltrichlorosilane – a reaction on which there fails to be any information in the literature.

We studied the chlorination and bromination of benzyltrichlorosilane under different temperature conditions (70-120°), at various molar ratios of silane and halide, and both in the absence and presence of catalysts (metallic iron, $SbCl_3$). It was established that in contrast to phenyltrichlorosilane the reaction with benzyltrichlorosilane, even in the presence of catalysts, proceeds without cleavage of the C–Si bond, despite the prolonged action of excess halide and elevated temperatures (100-120°), and leads to the formation of only the corresponding substitution products of benzyltrichlorosilane. Such behavior for the benzyltrichlorosilane in the examined reactions is explained by the presence of a methylene bridge between the Si atom and the aromatic ring, i. e., by the fact that the C–Si bond in benzyltrichlorosilane is aliphatic. A similar bond between silicon and carbon, as is known from the halogenation of aliphatic silanes, does not suffer rupture under the influence of either chlorine or bromine [5]. Such a bond also fails to cleave under the influence of $AlCl_3$ [6]. These circumstances permit obtaining in good yields without any complications the whole gamut of chloro- and bromo-derivatives of benzyltrichlorosilane, ranging from the mono- to the pentachloro(bromo)-nuclear-substituted derivatives.

In Table 1 we present data on the influence of catalysts, ratios of reactants, and temperature on the results of chlorinating and brominating benzyltrichlorosilane.

All five chloro- and five bromo-derivatives of benzyltrichlorosilane (with the halogens in the aromatic ring) were isolated in the pure state, and the physical and chemical characteristics are given for all of them.

The mono-, di-, tri-, tetrachloro- and bromo-derivatives of benzyltrichlorosilane are colorless oily liquids, the viscosities of which increase in measure with increase in the degree of chlorination. The pentachloro- and pentabromobenzyltrichlorosilanes are crystalline substances, difficultly soluble in ether and readily soluble in toluene and methylene chloride; they fail to burn in an open flame.

Their oxidation with nitric acid [7] to the corresponding chloro- and bromo-substituted benzoic acids was used to determine the structure of the described chloro- and bromo-derivatives of benzyltrichlorosilane. The structure of most of the former is known, and this allowed us, by identifying the obtained oxidation products, to judge both as to the position of the halogen atoms with respect to each other in the aromatic ring of the halobenzyltrichlorosilanes, and as to the orientation effect exerted by the $-CH_2SiCl_3$ group.

TABLE 1

Influence of Catalysts (Fe or $SbCl_3$), Reactant Ratios and Temperature on the Chlorination and Bromination of Benzyltrichlorosilane

Expt. Nos.	Halogenation conditions: halide	molar ratio $C_6H_5CH_2SiCl_3$/halide	amount of catalyst (in wt. % of silane taken	temperature	Total yield of reaction products (in %)	Main reaction product
1	Cl_2	1 : 0.9	0.5	50— 70°	71.7	Mono-
2		1 : 1.66	0.5	50— 75	76.5	Di-
3		1 : 3.0	0.5	50— 75	75.5	Tri-
4		1 : 6.0	1.0	75—100	76.2	Tatra-
5		1 : 8.0	1.0	75—100	71.4	Penta-
6*		1 : 5.4	—	100	80.0	Mono-
7	Br_2	1 : 1.0	0.5	45— 70	90.5	Mono-
8		1 : 2.1	0.5	45— 75	96.1	Di-
9		1 : 3.3	0.5	60— 95	85.5	Tri-
10		1 : 5.3	0.5	80—100	79.0	Tatra-
11		1 : 7.6	0.65	80—120	73.5	Penta-

*Without catalyst.

Oxidation of the monochloro- and monobromo-derivatives, synthesized by the halogenation of benzyltrichlorosilane (in either the presence or absence of catalysts), gave the p-chloro- and p-bromobenzoic acids (in respective yields of 80 and 76.4%). This indicates that the obtained monohalobenzyltrichlorosilanes are the p-chloro- and p-bromo-isomers.

The reaction products of the oxidation of the trichloro- and tribromobenzyltrichlorosilanes proved to be the 2,4,6-trichloro- and tribromobenzoic acids.

Since the trichloro(bromo)benzyltrichlorosilane is a symmetrically substituted derivative, then evidently the di-, tetra- and pentachloro(bromo)-derivatives are respectively the 2,4-di-,2,3,4,6-tetra- and 2,3,4,5,6-pentachloro(bromo)benzyltrichlorosilanes.

As is known, the methyl group (in toluene) shows ortho-, para-orientation, while the $SiCl_3$ group (in phenyltrichlorosilane) shows meta-orientation.

What should be the orientation effect of the $-CH_2SiCl_3$ group in benzyltrichlorosilane? The answer to this question could first be sought in examining a number of compounds of the $C_6H_5CH_2X$ type, containing a meta-orienting substitutent X that is separated from the aromatic ring by a methylene bridge. In Table 2 we present some literature data on the directive influence of the indicated type of substituents (during nitration), both when they are found in the aromatic ring and when they are separated from it by a methylene group. It follows from these data (Table 2) that in most cases the transition from the phenyl to the benzyl derivatives results in either nearly complete loss or sharp reduction of the meta-orienting effect shown by the substituents, and ortho- and para-isomers predominate in the reaction products.

We observed a similar phenomenon also in the case of benzyltrichlorosilane. In contrast to phenyltrichlorosilane, the phenyl nucleus of which so deactivated the $SiCl_3$ group that this compound (in the absence of catalysts) failed to chlorinate even at 170-180°, the benzyltrichlorosilane is capable of reacting with chlorine even at room temperature, while at 100° it is converted into p-chlorobenzyltrichlorosilane in 80% yield at a total rate that is only several times slower than the catalyzed ($SbCl_3$, etc.) reaction.

EXPERIMENTAL

1. Preparation of monochlorobenzyltrichlorosilane. A stream of dry chlorine at a rate of 20 ml/min was passed at 50-70° for 1.5 hours into a mixture of 20.6 g of benzyltrichlorosilane (b. p. 103-105° at 15 mm

TABLE 2

Influence of Substituent Position on the Nature of its Orienting Effect (From the Data of [8])

Orienting group in the benzene ring	Percent of meta-nitro isomer
$-\overset{+}{As}(CH_3)_3$	98.0
$-CH_2\overset{+}{As}(CH_3)_3$	3.4
$-\overset{+}{P}(CH_3)_3$	100.0
$-CH_2\overset{+}{P}(CH_3)_3$	10.0
$-\overset{+}{N}(CH_3)_3$	100.0
$-CH_2\overset{+}{N}(CH_3)_3$	88.0
$-NO_2$	93.0
$-CH_2NO_2$	66.0

and d_{20}^{20} 1.2858) and 0.1 g of antimony trichloride (or iron powder). The total amount of chlorine passed was 5.7 g. After blowing with dry air the weight increase of the reaction mass was 2.5 g (as compared to 3.1 g, the amount required for chlorination to the monochloro derivative).

Vacuum-distillation of the chlorination products gave: 1st fraction, b. p. 102-125° at 15 mm, 3.4 g; 2nd fraction, b. p. 125-140° at 15 mm, 19.0 g. Redistillation of the 2nd fraction gave 17.0 g of liquid with b. p. 130-136° at 15 mm, which was the monochlorobenzyltrichlorosilane. Yield 71.7%, based on the benzyltrichlorosilane taken for reaction.

Monochlorobenzyltrichlorosilane is a colorless mobile liquid that fumes in the air, b. p. 133-135° at 15 mm, d^{20} 1.4005.

Found %: Cl (total)* 54.20, 54.40; Cl (hydrol) 41.12, 41.30. $C_7H_6ClSiCl_3$. Calculated %: Cl (total) 54.6; Cl (hydrol) 40.96.

To prove its structure the obtained monochlorobenzyltrichlorosilane was oxidized with 20% nitric acid at 190-200°. From the reaction products we isolated p-chlorobenzoic acid (80% yield), m. p. 237-238°. To identify the p-chlorobenzoic acid the latter was nitrated with fuming HNO_3, as a result of which 4-chloro-3-nitrobenzoic acid, m. p. 180-181°, was obtained.

These data indicated that the obtained monochlorobenzyltrichlorosilane is the 4-chloro isomer.

2. Preparation of dichlorobenzyltrichlorosilane. The benzyltrichlorosilane was chlorinated to the dichloro-derivative under the same conditions as were used to obtain the monochloro-derivative; only the amount of passed chlorine was correspondingly increased.

Into a mixture of 20.2 g of benzyltrichlorosilane and 0.1 g of antimony trichloride (or iron powder) was passed for ~ 3 hours a stream of dry chlorine at a rate of 20 ml/min, maintaining the temperature of the reaction mass at 50-55° during the first hour of chlorination, and then to the end at 70-75°. The amount of chlorine passed was 11.0 g. The weight increase of the reaction mass after blowing with air was 5.0 g (as compared to the 6.1 g required for chlorination to the dichloro-derivative). Vacuum-distillation of the chlorination products gave the following fractions: 1st, b. p. 125-145° at 15 mm, 7.0 g; 2nd, b. p. 145-158° at 15 mm, 16.0 g. Redistillation of the 2nd fraction gave 14.2 g of liquid with b. p. 150-155° at 15 mm, which was dichlorobenzyltrichlorosilane. Yield 54.0%, based on benzyltrichlorosilane taken for reaction.

Dichlorobenzyltrichlorosilane is a colorless mobile oily liquid that fumes in the air, b. p. 152-154° at 15 mm, d^{20} 1.4941.

Found %: Cl (total) 60.08, 60.17; Cl (hydrol) 36.18, 36.15. $C_7H_5Cl_2SiCl_3$. Calculated %: Cl (total) 60.27; Cl (hydrol) 36.16.

Taking into consideration the orienting influence shown by the $-CH_2SiCl_3$ group, ensuing from the data obtained in proving the structure of the mono- and trichlorobenzyltrichlorosilanes (see below), it follows that the obtained dichlorobenzyltrichlorosilane is the 2,4-dichloro isomer.

Redistillation of the 1st fraction gave 5.3 g of monochlorobenzyltrichlorosilane with b. p. 133-135° at 15 mm. The total yield of chlorobenzyltrichlorosilanes was 76.5%.

* "Total" chlorine was determined by the Carius method.

3. Preparation of Trichlorobenzyltrichlorosilane. Benzyltrichlorosilane (20.9 g) was chlorinated at 50-75° for 5 hours under the conditions described above. The amount of chlorine passed was 19.0 g. The weight increase of the reaction mass after blowing with air was 8.4 g (as compared to the 9.2 g required for chlorination to the trichloro-derivative). Vacuum-distillation of the chlorination products gave the fractions: 1st, b. p. 145-160° at 15 mm, 7.6 g; 2nd, b. p. 160-175° at 15 mm, 18.4 g.

Redistillation of the 2nd fraction gave 16.0 g of liquid with b. p. 167-172° at 15 mm, which was trichlorobenzyltrichlorosilane. The yield was 53.1%, based on benzytrichlorosilane taken for reaction.

Trichlorobenzyltrichlorosilane is a colorless mobile oily liquid that fumes in the air, b. p. 169-171° at 15 mm, d^{20} 1.5740.

Found %: Cl (total) 64.63, 64.49; Cl (hydrol.) 32.43, 32.83. $C_7H_4Cl_3SiCl_3$. Calculated %: Cl (total) 64.74, Cl (hydrol.) 32.37.

Redistillation of the 1st fraction gave 5.9 g of dichlorobenzyltrichlorosilane with b. p. 151-154° at 15 mm. The total yield of chlorobenzyltrichlorosilanes was 75.5%.

To prove its structure the obtained trichlorobenzyltrichlorosilane was oxidized with 20% nitric acid. 2,4,6-Trichlorobenzoic acid (78.7% yield), m. p. 159-160°, was isolated from the reaction products. To identify it the 2,4,6-trichlorobenzoic acid was nitrated, as a result of which 2,4,6-trichloro-3-nitrobenzoic acid with m. p. 169° was obtained. These data indicate that the trichlorobenzyltrichlorosilane is the 2,4,6-trichloro isomer.

4. Preparation of Tetrachlorobenzyltrichlorosilane. Further chlorination of the benzyltrichlorosilane proceeded at a higher temperature and considerably slower rate than for the first three stages.

Into a mixture of 20.2 g of benzyltrichlorosilane and 0.2 g of antimony trichloride (or iron powder) was passed a stream of dry chlorine for 10 hours at a rate of 20 ml/min, keeping the temperature of the reaction mixture at 75-80° for the first two hours, and then to the end at 95-100°. The amount of chlorine passed was 38.0 g. The weight increase of the reaction mass after blowing with air was 12.5 g (as compared to the 12.25 g required for chlorination to the tetrachloro-derivative). Vacuum-distillation of the chlorination products gave the fractions: 1st, b. p. 166-190° at 15 mm, 3.1 g; 2nd, b. p. 190-205° at 15 mm, 24.0 g.

Redistillation of the 2nd fraction gave 22.5 g of liquid with b. p. 195-200° at 15 mm, which was tetrachlorobenzyltrichlorosilane. The yield was 69.4%, based on the benzyltrichlorosilane taken for reaction.

Tetrachlorobenzyltrichlorosilane is a colorless mobile oily liquid that fumes in the air, b. p. 196-198° at 15 mm, d^{20} 1.6386.

Found %: Cl (total) 67.98, 68.26; Cl (hydrol.) 29.58, 30.15. $C_7H_3Cl_4SiCl_3$. Calculated %: Cl (total) 68.36; Cl (hydrol.) 29.29.

Redistillation of the 1st fraction gave ~ 2.0 g of trichlorobenzyltrichlorosilane with b. p. 167-170° at 15 mm. The total yield of chlorobenzyltrichlorosilanes was 76.2 %.

5. Preparation of Pentachlorobenzyltrichlorosilane. The chlorination of the benzyltrichlorosilane to the pentachloro-derivative was run under the same conditions as for the tetrachloro-derivative, only the amount of chlorine passed was correspondingly increased. The preparation of the pentachlorobenzyltrichlorosilane required treating the benzyltrichlorosilane with excess chlorine at elevated temperature.

Into a mixture of 19.8 g of benzyltrichlorosilane and 0.2 g of antimony trichloride (or iron powder) was passed for 13 hours a stream of dry chlorine at a rate of 20 ml/min, at 75-80° for the first three hours and then at 95-100° to the end of reaction. The amount of chlorine passed was 49.4 g. The weight increase of the reaction mass after blowing with air was 14.1g (as compared to the 15.3 g required for chlorination to the pentachloro-derivative). The chlorination product crystallized (as needles) in measure with cooling. When vacuum-distilled the following fractions were obtained: 1st, b. p. 150-205° at 15 mm, 10.0 g; 2nd, b. p. 205-225° at 15 mm, 20.6 g. Redistillation of the 2nd fraction gave 18.4 g of clear colorless (when heated) liquid with b. p. 185-190° at 7 mm, which crystallized to a solid on cooling, being pentachlorobenzyltrichlorosilane. Yield 52.4%, based on benzyltrichlorosilane taken for reaction.

Pentachlorobenzyltrichlorosilane is a white crystalline substance, b. p. 186-187° at 7 mm, difficultly soluble in ether and acetone, readily soluble in toluene and methylene chloride, and failing to burn in an open flame. It is obtained as needles with m. p. 89-90° when recrystallized from ether.

Found %: Cl (total) 71.16, 71.44; Cl (hydrol.) 26.0, 26.34; $C_7H_2Cl_5SiCl_3$. Calculated %: Cl (total) 71.35; Cl (hydrol.) 26.76.

Redistillation of the 1st fraction gave 6.1 g of liquid with b. p. 195-200° at 15 mm, which is the tetrachlorobenzyltrichlorosilane. The total yield of polychlorobenzyltrichlorosilanes was 71.4%.

6. Preparation of Monobromobenzyltrichlorosilane. To a mixture of 19.5 g of benzyltrichlorosilane and 0.1 g of antimony trichloride (or iron powder) was added in drops 15.0 g of dry bromine in 0.5 hour at room temperature. On conclusion of adding all of the bromine, to complete the reaction, the reaction mass was heated for 20 minutes at 70°, after which it was blown with dry air to remove traces of hydrogen bromide. The weight increase of the reaction mass after blowing was 7.1 g (as compared to the 6.8 g required for bromination to the monobromo-derivative). Vacuum-distillation of the bromination products gave a fraction with b. p. 133-140° at 10 mm, weight 25.2 g. Redistillation of this fraction gave 23.8 g of colorless liquid with b. p. 137-139° at 10 mm, which was the monobromobenzyltrichlorosilane. Yield 90.5%, based on benzyltrichlorosilane taken for reaction.

Monobromobenzyltrichlorosilane is a colorless mobile oily liquid that fumes in the air, b. p. 137-138° at 10 mm, d^{20} 1.6076. To determine the bromine content a small portion of the obtained monobromobenzyltrichlorosilane was converted into a resin by treatment with water, which was then analyzed.

Found %: Br 35.7, 35.9; Cl (hydrol.) 34.87, 34.83. $C_7H_6BrSiO_{1.5}$. Calculated %: Br 36.03. $C_7H_6BrSiCl_3$. Calculated %: Cl (hydrol.) 34.97.

To prove its structure the obtained monobromobenzyltrichlorosilane was oxidized with 20% nitric acid. From the reaction products we isolated p-bromobenzoic acid (yield 76.4%), m. p. 250-251°. For identification the p-bromobenzoic acid was nitrated, as a result of which 4-bromo-3-nitrobenzoic acid was obtained, m. p. 198-199°. On the basis of these data it follows that the obtained monobromobenzyltrichlorosilane is the 4-bromo isomer.

7. Preparation of dibromobenzyltrichlorosilane. The benzyltrichlorosilane was brominated to the dibromo-derivative under the above-described conditions; only the amount of bromine introduced into reaction was correspondingly increased. To a mixture of 20 g of benzyltrichlorosilane and 0.1 g of $SbCl_3$ (or iron powder) was added in drops at 45-50° and with stirring, 30.9 g of dry bromine in 1 hour and 40 minutes, after which, to complete the reaction, the reaction mass was heated for 1 hour at 70-75°. The weight increase of the reaction mass after blowing with air was 15.0 g (as compared to the 14.0 g required for bromination to the dibromo-derivative). Vacuum-distillation of the bromination products gave the fractions: 1st, b. p. 135-145° at 10 mm, 4 g; 2nd, b. p. 145-169° at 10 mm, 3.0 g; 3rd, b. p. 169-175° at 10 mm, 25.0 g.

The first fraction was monobromobenzyltrichlorosilane. Redistillation of the 3rd fraction gave 23.3 g of colorless liquid with b. p. 169-173° at 10 mm, which was the dibromobenzyltrichlorosilane. Yield 70.0%, based on benzyltrichlorosilane taken for reaction (total yield of bromo-derivatives was 96.1%).

Dibromobenzyltrichlorosilane is a colorless mobile oily liquid that fumes in the air, b. p. 170-172° at 10 mm, d^{20} 1.8872. To determine the bromine content a small portion of this liquid was converted to a resin by treatment with water, which was then analyzed.

Found %: Br 52.60, 52.80; Cl (hydrol.) 28.09, 27.78. $C_7H_5Br_2SiO_{1.5}$. Calculated %: Br 53.15. $C_7H_5Br_2SiCl_3$. Calculated %: Cl (hydrol.) 27.77.

Oxidation of the obtained dibromobenzyltrichlorosilane with 20% nitric acid gave the 2,4-dibromobenzoic acid (yield 77.2%), m. p. 169-170°. For identification the 2,4-dibromobenzoic acid was treated with phosphorus pentachloride, as a result of which the acid chloride with m. p. 50° was obtained. On the basis of the presented data it follows that the obtained dibromobenzyltrichlorosilane is the 2,4-dibromo isomer.

8. Preparation of Tribromobenzyltrichlorosilane. To a mixture of 21 g of benzyltrichlorosilane and 0.1 g of $SbCl_3$ (or iron powder) was gradually added 49.3 g of dry bromine in 4 hours and 10 minutes. The first half

of the bromine was added at 60°, and the second half at 70-80°, after which the reaction mixture was heated for 1 hour at 90-95° to complete the reaction. The weight increase of the reaction mass after blowing with air was 22.8 g (as compared to the 22.0 g required for bromination to the tribromo-derivative). Vacuum-distillation of the bromination products gave the fractions: 1st, b. p. 160-190° at 10 mm, 6.4 g; 2nd, b. p. 190-196° at 10 mm, 30.8 g.

The 1st fraction was a mixture of the di- and tribromo-derivatives of benzyltrichlorosilane. Redistillation of the 2nd fraction gave 28.7 g of colorless liquid with b. p. 193-196° at 10 mm, being the tribromobenzyltrichlorosilane. Yield 60.7%, based on the benzyltrichlorosilane taken for reaction (total yield of bromo-derivatives was ~ 85.5%).

Tribromobenzyltrichlorosilane is a colorless mobile oily liquid that fumes in the air, b. p. 195-196° at 10 mm, d^{20} 2.1260. To determine its bromine content a small portion of the tribromo-derivative was treated with water to give a resin, which was then analyzed.

Found %: Br 62.40, 62.91; Cl (hydrol.) 22.62, 22.35. $C_7H_4Br_3SiO_{1.5}$. Calculated %: Br 63.16. $C_7H_4Br_3SiCl_3$. Calculated %: Cl (hydrol.) 23.02.

The oxidation of the tribromobenzyltrichlorosilane with 20% nitric acid gave 2,4,6-tribromobenzoic acid (79.8% yield), m. p. 187-188°, which for identification purposes was converted (by reaction with PCl_5) to the acid chloride, m. p. 47-48°. The obtained data indicated that the tribromobenzyltrichlorosilane, formed in the reaction of benzyltrichlorosilane with bromine, is the 2,4,6-tribromo isomer.

9. Preparation of Tetrabromobenzyltrichlorosilane. Similar to the chlorination, further bromination of the benzyltrichlorosilane proceeded considerably slower than did the first three stages, and required the use of both elevated temperature and an excess of bromine.

To a mixture of 15.6 g of benzyltrichlorosilane and 0.075 g of iron powder was added in drops and with stirring 60.0 g of dry bromine in 5 hours and 15 minutes at 80-85°. On conclusion of adding all of the bromine the reaction mass was heated for 1 hour at 95-100° to complete the reaction. The weight increase of the reaction mass after blowing with air was 21.1 g (as compared to the 21.8 g required for bromination to the tetrabromo-derivative). Vacuum-distillation of the bromination products gave the fractions: 1st, b. p. 190-215° at 10 mm, 9.3 g; 2nd, b. p. 215-227° at 10 mm, 20.6 g.

The 1st fraction was a mixture of the tri- and tetrabromo-derivatives of benzyltrichlorosilane. Redistillation of the 2nd fraction gave 18.1 g of colorless viscous liquid with b. p. 219-223° at 10 mm, being the tetrabromobenzyltrichlorosilane. Yield ~ 50 %, based on benzyltrichlorosilane taken for reaction (total yield of bromo-derivatives ~ 79.0 %).

Tetrabromobenzyltrichlorosilane is a slow-flowing viscous colorless liquid that fumes in the air, b. p. 220-222° at 10 mm, d^{20} 2.2586. The bromine content was determined in the resin that was obtained from the hydrolysis of this liquid.

Found %: Br 69.06, 69.39; Cl (hydrol.) 19.34, 19.40. $C_7H_3Br_4SiO_{1.5}$. Calculated %: Br 69.71. $C_7H_3Br_4SiCl_3$. Calculated %: Cl (hydrol.) 19.66.

10. Preparation of Pentabromobenzyltrichlorosilane. The bromination of the benzyltrichlorosilane to the pentabromo-derivative was run under the conditions of prolonged exposure of the benzyltrichlorosilane to the action of excess bromine at elevated temperature.

To a mixture of 15.0 g of benzyltrichlorosilane and 0.1 g of iron powder was gradually added 80.0 g of dry bromine in 10 hours. The first 40.0 g of bromine was added at 80-90°, and the second 40 g at 110-120°. After all of the bromine had been added the reaction mixture was heated for 2 hours at 120° to complete the reaction. The weight increase of the reaction mass after blowing with air was 25.1 g (as compared to the 26.2 g required for bromination to the pentabromo-derivative). The bromination product crystallized as it cooled. Its vacuum-distillation gave the fractions: 1st, b. p. 200-230° at 4 mm, 4.1 g; 2nd, b. p. 230-238° at 4 mm, 29.0 g.

The 1st fraction was a mixture of the tetra- and pentabromo-derivatives of benzyltrichlorosilane. Redistillation of the 2nd fraction gave 25.6 g of clear (when heated) colorless liquid with b. p. 233-236° at 4 mm, rapidly changing to a solid as it cooled, and being the pentabromobenzyltrichlorosilane. Yield 62.1%, based on benzyltrichlorosilane taken for reaction (total yield of bromo-derivatives ~ 73.5%).

Pentabromobenzyltrichlorosilane is a white crystalline substance, b. p. 234-236° at 4 mm, needles (from ether), m. p. 120-121°. The bromine content was determined in the resin that was obtained from the hydrolysis of this compound.

Found %: Br 73.82, 74.08; Cl (hydrol.) 16.7; 16.8. $C_7H_2Br_5SiO_{1.5}$. Calculated %: Br 74.34. $C_7H_2Br_5SiCl_3$. Calculated %: Cl (hydrol.) 17.16.

11. Preparation of p-Chlorobenzyltrichlorosilane by the Thermal Chlorination of Benzyltrichlorosilane in the Absence of Catalysts. Here 18.0 g of benzyltrichlorosilane was chlorinated at 100° for 8 hours (chlorine rate 20 ml/min). The total amount of chlorine passed was 30.4 g. The weight increase of the reaction mass after blowing with air was 2.6 g (as compared to the 2.7 g required for chlorination to the monochloro-derivative). Vacuum-distillation of the chlorination products gave: 1st fraction, b. p. 100-128° at 15 mm, 1.5 g; 2nd fraction, b. p. 128-137° at 15 mm, 18.0 g. Redistillation of the 2nd fraction gave 16.5 g of liquid with b. p. 132-135° at 15 mm and d^{20} 1.4010, which was the monochlorobenzyltrichlorosilane. Yield 80.0%, based on benzyltrichlorosilane taken for reaction.

Found %: Cl (hydrol.) 41.08, 41.27. $C_7H_6ClSiCl_3$. Calculated %: Cl (hydrol.) 40.96.

The monochlorobenzyltrichlorosilane was oxidized with 20% nitric acid. Here p-chlorobenzoic acid was isolated, which was identified as its nitro derivative, m. p. 181°. Its mixed melting with synthetic p-chlorobenzoic acid revealed no depression of melting point (237-238°).

SUMMARY

1. It was established that the chlorination and bromination of benzyltrichlorosilane in the presence of the usual catalysts for the halogenation of aromatic compounds (iron, $SbCl_3$) can lead to a whole gamut of nuclear halo-substituted chloro- and bromo-derivatives of benzyltrichlorosilane, ranging from the monochloro(bromo)- to the pentachloro(bromo)-derivative.

2. The chlorination and bromination of benzyltrichlorosilane in the presence of the above-indicated catalysts proceeds without cleavage of the C—Si bond, since the latter is an aliphatic bond.

3. All 5 of the chloro- and bromo-derivatives of benzyltrichlorosilane were isolated in the pure state and then characterized.

4. The structure of all of the chlorination and bromination products of benzyltrichlorosilane was shown, and it was established that the monochloro(bromo)-derivative is the 1,4-isomer, the dichloro(bromo)-derivative is the 1,2,4-isomer, the trichloro(bromo)-derivative is the 1,2,4,6-isomer, the tetrachloro(bromo)-derivative is the 1,2,3,4,6-isomer, and the pentachloro(bromo)-derivative is the 1,2,3,4,5,6-pentachloro(bromo)benzyltrichlorosilane.

5. It was found in the halogenation of benzyltrichlorosilane, both in the presence and absence of catalysts that the $-CH_2SiCl_3$ group orients the halogen atoms entering the aromatic nucleus to the ortho-, para-positions.

LITERATURE CITED

[1] A. Ya. Yakubovich and G. V. Motsarev, Proc. Acad. Sci. USSR 91, 277 (1953); 99, 1015 (1954).

[2] A. Ya. Yakubovich and G. V. Motsarev, J. Gen. Chem. 23, 412 (1953) (T. p. 421).*

[3] A. Ya. Yakubovich and G. V. Motsarev, J. Gen. Chem. 26, 586 (1956) (T. p. 611).*

[4] A. Ya. Yakubovich and G. V. Motsarev, J. Gen. Chem. 26, 1413 (1956) (T. p. 1593).*

[5] W. F. Gilliam and R. O. Sauer, J. Am. Chem. Soc. 67, 1810 (1945); F. C. Whitmore and L. H. Sommer, J. Am. Chem. Soc. 68, 481 (1946).

*T. p. = C. B. Translation pagination.

[6] R. Benkeser and H. Kryslak, J. Am. Chem. Soc. 76, 599 (1954); A. D. Petrov, E. A. Chernyshev and I. A. Kulish, Proc. Acad. Sci. USSR 100, 929 (1955).

[7] I. N. Nazarov, N. V. Kuznetsov and A. V. Semenovsky, Proc. Acad. Sci. USSR 99, 1003 (1954).

[8] C. K. Ingold, Rec. trav. chim. 48, 805 (1929).

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ESTERS OF N-PHOSPHORIC ACID, TRICHLOROIMINOACETIC ACID AND ESTERS OF TRIHYDROXYPHOSPHAZOTRICHLOROACETYL

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Esters of types $RCON=P(OR')_3$ (I), $RC(OR')=NPO(OR')_2$ (II) have been unknown until now. The isomeric trichlorophosphazotrichloroacetyl, $CCl_3CON=PCl_3$ (III), and the N-phosphoryl chloride of trichloroiminoacetyl chloride, $CCl_3CCl=NPOCl_2$ (IV) [1], when treated with alcoholates and phenolates should give two series of corresponding triesters, and specifically: the triesters of trihydroxyphosphazotrichloroacetyl chloride (Type I), $CCl_3CON=P(OR)_3$ (V), and the triesters of the N-phosphoric acid of trichloroiminoacetic acid (Type II)–$CCl_3C(OR)=NPO(OR)_2$ (VI). The preparation of these esters and a comparison of their properties, both between themselves and with those of the recently obtained trihydroxyphosphazosulfonyl esters of the type of $RSO_2N=P(OR')_3$ [2], is of undoubted interest. In addition, the preparation and study of the chemical properties of esters (V) and (VI) is conclusive proof of the validity of the trichlorophosphazotrichloroacetyl structure, and consequently, of all of the other trichlorophosphazoacyls [1, 4].

Only one attempt to prepare esters of the (I) type has been described in the literature. Steinkopf [3] studied the reaction products of alcohols and alcoholates with chloride (III) (which he erroneously assumed to be chloride (IV) [1]), but he was able to obtain only the diesters of trichloroacetylamidophosphoric acid, $CCl_3CONHPO(OR)_2$, since the alkoxylation of chloride (III) under the reaction conditions employed by Steinkopf was always accompanied by the replacement of one chlorin atom by hydroxyl.

Using the methods developed earlier for the alkoxylation of trichlorophosphazosulfonyl compounds [2] for chlorides (III) and (IV), we were able to obtain the corresponding triesters of the types of (V) and (VI), although not in all cases. The triphenyl esters $CCl_3CON=P(OC_6H_5)_3$ (VII) and $CCl_3C(OC_6H_5)=NPO(OC_6H_5)_2$ (VIII) were studied in greatest detail. Both of them are colorless liquids that fail to distill without decomposition, (VII) being mobile, and (VIII) being very viscous. Their densities and specific refractivities proved to be quite close, and consequently it was necessary to prove their difference as chemical compounds, since it could be assumed that isomerization occurs in the phenoxylation of one of the chlorides (III) and (IV), and as a result the same product is obtained. Both esters (VII) and (VIII) are saponified with the formation of the diphenyl ester of trichloroacetylamidophosphoric acid, the structure of which is shown by its synthesis from trichloroacetylamidophosphorylchloride, in accord with the schemes:

$$\left.\begin{array}{l} CCl_3CON=P(OC_6H_5)_3 + H_2O \\ CCl_3C(OC_6H_5)=NPO(OC_6H_5)_2 + H_2O \\ CCl_3CONHPOCl_2 + 2NaOC_6H_5 \end{array}\right\} \rightarrow CCl_3CONHPO(OC_6H_5)_2.$$

However, this saponification proceeds at an entirely different rate for the two esters. Ester (VIII) is saponified many times more rapidly than is ester (VII). The shaking of ester (VIII) with the theoretical amount of 1 N sodium hydroxide solution at room temperature results in its complete saponification in 15 minutes. Ester (VII) is saponified only after boiling for 90 minutes. When 0.2 N sodium hydroxide solution is added at 0° to an alcohol solution of (VIII) the latter titrates practically instantaneously and quantitatively as a monobasic acid; (VII) under the same conditions titrates at a rate of about 0.2 ml of 0.2 N sodium hydroxide solution in 5 minutes.

in which connection the saponification stops after approximately 50% of the theoretical amount of alkali has been added (see Experimental for the explanation of this phenomenon). (VIII) is also saponified by atmospheric moisture at an incomparably faster rate than is (VII) (see Experimental).

The (VII) and (VIII) behave in an entirely different manner when subjected to thermal cleavage, proceeding in accord with the schemes:

$$CCl_3CON{=}P(OC_6H_5)_3 \rightarrow CCl_3CN + PO(OC_6H_5)_3,$$

$$CCl_3C(OC_6H_5)N{=}PO(OC_6H_5)_2 \rightarrow CCl_3CN + \text{resinous products}.$$

Both esters begin to cleave at 245-250°, and decomposition is complete after 50 minutes at 300°. Here ester (VII) gives 78.5% of trichloroacetonitrile and 74.4% of triphenyl phosphate, while ester (VIII) gives only 41.5% of acetonitrile. We were unable to isolate triphenyl phosphate from the thermal cleavage products of (VIII).

As a result, it can be assumed as rigidly proven that (VII) and (VIII) are different isomers with completely different chemical properties, and that in thermal cleavage of the indicated type the phenoxyl group fails to "skip over" to the phosphorus atom, which had only been assumed earlier [5].

When esters of the $RSO_2N{=}P(OR')_3$ (IX) type are compared with esters (VII) and (VIII), and with other similarly constructed compounds, it can be stated that: 1) all of the esters of the $AcN{=}P(OR)_3$ type are quite easily saponified by alkalies, being converted into diesters of the corresponding acylamidophosphoric acids; 2) of them the ones that are most difficult to saponify are the type (IX) esters, esters of the (V) type are saponified with considerably greater ease, while those of the (VI) type are saponified with exceptional ease; evidently, esters of the (VI) type should be active alkylation agents, probably, even more active than dimethyl sulfate; thermal cleavage with the formation of the corresponding nitrile and corresponding phosphoric acid derivative proceeds most easily for the aromatic trichlorophosphazoacyls [4], it also proceeds easily for the type (I) esters, derived from aromatic acids [5], with slightly greater difficulty for the phosphazosulfonyl chloride [4], with considerably greater difficulty for the (V) type of esters [for example (VII)] and chlorides (III) and (IV) [1], and is practically at a standstill for the (VI) type of esters (for example VIII).

Besides (VII), of the (V) type of esters we prepared the tri-p-chlorophenoxyphosphazotrichloroacetyl, $CCl_3CON{=}P(OC_6H_4Cl\text{-}p)_3$ (X), a thick viscous liquid, and the triethoxyphosphazotrichloroacetyl, $CCl_3CON{=}P(OC_2H_5)_3$ (XI), a mobile liquid of disagreeable odor. (X) is also easily saponified the same as (VIII), and (XI) is saponified even more easily. We were unable to isolate trimethoxyphosphazotrichloroacetyl (XII) – its formation was noticed only by the disagreeable odor of the reaction mixture. Instead of (XII), the sodium salt of the dimethyl ester of trichloroacetylamidophosphoric acid was obtained in nearly quantitative yield. Its formation is probably due to chloride (III) reacting not only with sodium methylate, but also with free methyl alcohol, in accord with the scheme:

$$CCl_3CON{=}PCl_3 + 2CH_3ONa + CH_3OH \rightarrow CH_3CONHPO(OCH_3)_2 + CH_3Cl,$$
$$CCl_3CONHPO(OCH_3)_2 + CH_3ONa \rightarrow CCl_3CONaPO(OCH_3)_2 + CH_3OH.$$

When hydrolyzed with alkalies in aqueous-alcohol solution all three esters (VII), (X) and (XI) easily give the corresponding diesters of trichloroacetylamidophosphoric acid (XIII) in good yields. These same esters are also obtained in good yields from the trichloroacetylamidophosphoryl dichloride (XIV) by reaction with sodium ethylate and sodium arylates, in which manner their structure is proved. In some cases the esters of type (XIII) are obtained from (XIV) and arylates in very poor yields; in such case they can be obtained from (III) and the corresponding arylates, without isolation of the easily hydrolyzed esters of the (V) type. The di-o-nitro- and di-p-nitrodiphenyl esters of trichloroacetyiamidophosphoric acid were obtained in this manner. All of the esters of type (XIII) are crystalline, comparatively high-melting compounds, quantitatively titrating with alkalies as monobasic acids with the formation of salts that crystallize well.

When reacted with phosphorus pentachloride the diesters of the type of (XIII) give in quantitative yield the diesters of the N-phosphoric acid of trichloroiminoacetyl chloride in accord with the scheme:

$$CCl_3CONHPO(OR)_2 + PCl_5 \rightarrow POCl_3 + HCl + CCl_3CCl{=}NPO(OR)_2.$$

Thus, for example, the reaction of the diphenyl ester of trichloroacetylamidophosphoric acid with phosphorus pentachloride gives in quantitative yield the diphenyl ester of the N-phosphoric acid of trichloroiminoacetyl chloride, $CCl_3CCl{=}NPO(OC_6H_5)_2$, a colorless mobile liquid, hydrolyzed with exceeding ease by water, and being almost quantitatively converted into the starting ester. Besides (VIII), of the esters of type (VI) we prepared the tri-p-chlorotriphenyl ester of the N-phosphoric acid of trichloroiminoacetic acid (XV), being a thick, very viscous liquid. (XV) is saponified with even greater ease than is (VIII).

EXPERIMENTAL

Triphenoxyphosphazotrichloroacetyl (VII). To a solution of 0.35 mole of trichlorophosphazotrichloroacetyl chloride in 100.0 ml of benzene with vigorous stirring was rapidly added 0.106 mole of well-dried, finely-ground sodium phenolate (12.3 g). The reaction was highly exothermic. After 10-15 minutes, with continous stirring, the mixture was heated to 70-80° for 20-30 minutes. The sodium chloride precipitate was removed by centrifuging (filtration is exceedingly slow), the benzene solution was cooled to 0°, washed at 0° with 100 ml of 1 N sodium hydroxide solution, and filtered successively through two funnels, one situated over the other, using filters each containing 5.0 g of anhydrous sodium sulfate. The clear colorless benzene solution was immediately evaporated in vacuo at 6 mm, at first at room temperature, and toward the end at 60°. The residue contained the triphenoxyphosphazotrichloroacetyl as a quite mobile, colorless, transparent, odorless liquid, readily soluble in most organic solvents, and insoluble in water. Yield 73.3% (12.1 g).

d_4^{20} 1.31, n_D^{20} 1.638, R_D^{20} 0.348.

Found %: N 3.09. $C_{20}H_{15}O_4NPCl_3$. Calculated %: N 2.97.

Tri-p-chlorophenoxyphosphazotrichloroacetyl (X). The synthesis was run the same as for (VII); yield 69.8%. (X) is a colorless, transparent, viscous, odorless liquid, insoluble in water, and readily soluble in most organic solvents; n_D^{20} 1.782.

Found %: N 2.51. $C_{20}H_{12}O_4NPCl_6$. Calculated %: N 2.44.

Triethoxyphosphazotrichloroacetyl (XI). To a cooled 0° solution of 0.091 mole of sodium (2.1 g) in 50.0 ml of anhydrous ethyl alcohol with vigorous stirring and external cooling was added a solution of 0.03 mole of trichlorophosphazotrichloroacetyl (8.94 g) in 30.0 ml of benzene at such a rate that the temperature of the reaction mixture remained at 0-5°. Then the mixture was heated at 70-80° for 20-30 minutes, the sodium chloride removed by filtration, and the solvents vacuum-distilled. The obtained oily liquid (6.5 g, 65.8%) was stirred with 30.0 ml of benzene, the solution cooled to 0°, and then rapidly washed with 20.0 ml of 1 N sodium hydroxide solution at 0°. The benzene solution was rapidly dried over sodium sulfate and the benzene was vacuum-distilled, at first at room temperature, and toward the end at 60°. The triethoxyphosphazotrichloroacetyl obtained in this manner is a colorless, transparent, mobile liquid of disagreeable odor, readily soluble in most organic solvents; yield 2.5 g (25.7%).

d_4^{20} 1.24, n_D^{20} 1.598, R_D^{20} 0.352.

Found %: N 4.32. $C_8H_{15}O_4NPCl_3$. Calculated %: N 4.35.

The diethyl ester of the trichloroacetylamidophosphoric acid can be isolated in nearly quantitative yield from the aqueous alkali solutions, m. p. 46-47°, which agrees with the literature data [3].

Trimethoxyphosphazotrichloroacetyl (XII). We were unable to obtain (XII) in a similar manner, although its formation in small amount was detected by the very specific disagreeable odor of the reaction mixture, vanishing after vacuum-evaporation. The solitary isolated reaction product proved to be the sodium salt of the dimethyl ester of trichloroacetylamidophosphoric acid, being a microcrystalline colorless powder, readily soluble in water, m. p. 208-211°, yield 97.9%.

Found %: N 4.70. $C_4H_6O_4NPCl_3Na$. Calculated %: N 4.78.

Treatment of the sodium salt with hydrochloric acid gave the dimethyl ester of trichloroacetylamidophosphoric acid in 94.1% yield; the substance crystallizes from water as small plates with m. p. 105-107°, which agrees with the literature data [3].

Triphenyl Ester of the N-phosphoric acid of trichloroiminoacetic acid (VIII). To a solution of 0.02 mole of the N-phosphorylchloride of trichloroiminoacetyl chloride (5.96 g) in 60.0 ml of benzene was rapidly added with vigorous stirring 0.0604 mole of dry, well-ground sodium phenolate (7.00 g). The reaction mixture showed quite strong self-heating and assumed a light-yellow color. Stirring was continued until a drop of the mixture with a few drops of water failed to show acid to Congo, which required 20-25 minutes. Further treatment was the same as used for the preparation of (VII). Special attention has to be given to the cooling of the solutions and the washing with alkali, and to run all of the operations of washing and of drying the benzene solution as rapidly as possible, since the reaction product is saponified with extreme ease.

(VII) was obtained in 74.5% yield (7.0 g) and is a colorless, very viscous, odorless liquid, readily soluble in the ordinary organic solvents, d_4^{20} 1.34, n_D^{20} 1.561, R_D^{20} 0.313. On standing in the air or in contact with water it is very rapidly hydrolyzed, quantitatively decomposing into phenol and the diphenyl ester of trichloroacetylamidophosphoric acid. It is even more easily hydrolyzed when mixed with caustic alkali solutions (see below).

Found %: N 2.90. $C_{20}H_{15}O_4NPCl_3$. Calculated %: N 2.97.

Tri-p-chlorotriphenyl ester of the N-phosphoric acid of trichloroiminoacetic acid (XV). The compound was obtained in the same manner as (VIII). It is saponified even more easily than (VIII), for which reason its total yield was only 10-15% (1.0-1.5 g).

(XV) is a thick, very viscous, colorless, odorless liquid, n_D^{20} 1.710; it rapidly solidifies in the air, being transformed to the diester.

Found %: N 2.40. $C_{20}H_{12}O_4NPCl_6$. Calculated %: N 2.44.

The alkaline wash liquors were evaporated in vacuo to small volume, and the solution was made acid to Congo. Here the di-p-chlorodiphenyl ester of trichloroacetylamidophosphoric acid precipitated as a colorless microcrystalline powder, crystallizing from alcohol as small tablets, m. p. 132-133°; yield 62.8%; insoluble in water, difficultly soluble in alcohol, ether and petroleum ether, readily soluble in acetone and carbon tetrachloride, shows acid properties, and titrates as a monobasic acid in 50% alcohol solution, using phenolphthalein indicator.

Found: equiv. 1.01. $C_{14}H_9O_4NPCl_5$. Calculated: equiv. 1.00

The sodium salt was obtained by mixing the di-p-chlorodiphenyl ester of trichloroacetylamidophosphoric acid with the theoretical amount of sodium hydroxide solution and evaporating in vacuo; colorless microcrystalline powder, readily soluble in water, m. p. 196-198°.

Found %: N 2.82. $C_{14}H_8O_4NPCl_5Na$. Calculated %: N 2.88.

Comparative hydrolysis of triphenoxyphosphazotrichloroacetyl (VII) and of the triphenyl ester of the N-phosphoric acid (VIII). Hydrolysis with the theoretical amount of 1 N sodium hydroxide. A mixture of 0.01 mole of the substance (4.7 g) with 10.0 ml of 1 N sodium hydroxide solution was vigorously shaken. Here (VIII) completely dissolved after shaking for 15 minutes at room temperature. In order to effect complete solution of (VII) it was necessary to boil the mixture under reflux for 1.5 hours. The obtained solutions were evaporated in vacuo to dryness, the solid crystalline residue was washed twice with 3.0 ml portions of ether, and dried. The yield of the sodium salt of the diphenyl ester of trichloroacetylamidophosphoric acid from (VII) was 80.2% (3.33 g), and from (VIII) it was 72.5% (3.0 g), m. p. 213-214°; colorless microcrystalline powder, readily soluble in water.

Found %: N 3.30. $C_{14}H_{10}O_4NPCl_3Na$. Calculated %: N 3.33.

Treatment of the salt with hydrochloric acid gave the diphenyl ester of trichloroacetylamidophosphoric acid; the yield was nearly quantitative, m. p. 101-102°; the compound was identified by its mixed melting point.

Hydrolysis with atmospheric moisture. The same weight samples (~ 0.5 g) of (VII) and (VIII) and a phenol sample (~ 0.3 g), mixed with ground glass, were placed on watch glasses. All three watch glasses with samples were placed in a ventilated area, protected from dust, at a room temperature of + 18, + 25°. The phenol evaporated completely in three days. (VIII) after a day was a compact mass of crystals, while (VII) remained clear for two days and it was only on the third day that individual crystals began to form. During two days the substances on the watch glasses were stirred with glass rods to facilitate admittance of atmospheric moisture. The weight loss of substance (VIII) after a day was 2.4% of the total weight (14.8% of the theoretical), after two days it was 3.0% (18.5% of the theoretical), and after 10 days it was 14.7% (90.9% of the theoretical). The weight loss of substance (VII) after a day was a total of only 0.25% (1.55% of the theoretical), after two days it was 0.35% (2.17% of the theoretical), and after 10 days it was 9.5% (58.8% of the theoretical).

Titration with sodium hydroxide in aqueous-alcohol solution at 0°. In 25.0 ml of ethyl alcohol, cooled to 0°, were dissolved 0.001 mole of (VII) and of (VIII) (0.4705 g). Both solutions were titrated at 0° with 0.2 N sodium hydroxide solution in the presence of phenolphthalein. (VIII) titrated almost instantaneously as a monobasic acid. – a pink color appeared after the addition of 5.0 ml of 0.2 N sodium hydroxide solution. The solvent was vacuum-distilled to dryness, and the crystalline residue was washed twice with 3.0 ml portions of ether. The yield of the sodium salt of the diphenyl ester of trichloroacetylamidophosphoric acid was 98.0% (0.405 g), m. p. 213-214°: it was identified by treatment with hydrochloric acid to give the free ester.

(VII) titrated slowly, at a rate of approximately 0.2 ml of 0.2 N sodium hydroxide solution in 5 minutes. After about 50% of the alkali had been added the pink color failed to disappear after 4 hours at 0°. Removal of the alcohol by distillation and washing with ether gave about a 50% yield (0.2 g) of the sodium salt of the diphenyl ester of trichloroacetylamidophosphoric acid.

As a result, the saponification of (VIII) in aqueous-alcohol solution at 0° and with a very small concentration of alkali is practically instantaneous, despite the fact that toward the end of reaction there is a large excess of free phenol in the solution, lowering the solution pH. In other words, substance (VIII) is easily saponified not by sodium hydroxide, but by sodium phenolate.

The saponification of (VII) under these conditions is incomparably slower, and when a considerable amount of phenol accumulates in solution the saponfication practically ceases. However, at the boiling point of water, (VII) is hydrolyzed with comparative ease by sodium phenolate (see above).

Thermal cleavage of triphenoxyphosphazotrichloroacetyl (VII) and of the triphenyl ester of the N-phosphoric acid of trichloroiminoacetic acid (VIII). The substance was placed in a Claisen flask, fitted with two thermometers and connected to a straight condenser and receiver. The bulb of one of the thermometers was in the substance, while the bulb of the other thermometer was in the vapors of the distilling liquid. The heating was done on an air bath. (VII) began to decompose (boil) to a liquid at 245°. The temperature was gradually raised. Trichloroacetonitrile began to distill at a vapor temperature of 74-95°. After 50 minutes, at 300°, the liquid turned dark, and the evolution of trichloroacetonitrile ceased. The receiver was changed, the apparatus was connected to a vacuum source and the triphenyl phosphate was distilled at 175-233° and 5 mm. The major portion distilled at 230°. From 0.037 mole of (VII) (17.65 g) we obtained: 78.5% of trichloroacetonitrile (4.2 g), 74.4% of triphenyl phosphate (9.3 g), and 3.25 g of carbonaceous residue in the flask (18.4%) with 0.9 g of losses (5.1%). After distillation through a short column the trichloroacetonitrile was identified by its boiling point, specific gravity and refraction; after recrystallization the triphenyl phosphate was identified by its mixed melting point.

(VIII) began to decompose at 250°. Its decomposition into a liquid was ended after 50 minutes at 300°. From 0.015 mole of (VIII) (7.05 g) we obtained: 41.6% of acetonitrile (0.9 g), 0.8 g of liquid distillate that failed to crystallize, with b. p. about 160° at 5 mm (11.3%), and 4.95 g of carbonaceous residue (70.3%) with 0.4 g of losses (5.7%). We were unable to isolate triphenyl phosphate.

Hydrolysis of triethoxy- (XI), triphenoxy- (VII) and tri-p-chlorotriphenoxy- (X) phosphazotrichloroacetyls. A mixture of 0.0075 mole of the substance with 40.0 ml of alcohol and 10.0 ml of 1 N sodium hydroxide solution was boiled for 1 hour. The alcohol was distilled off and hydrochloric acid was added to the residue until acid to Congo. The resulting crystals were separated, washed with water and 0.5 ml of ether, and dried. The yield of the diphenyl ester of trichloroacetylamidophosphoric acid was 64.2% (2.0 g); after recrystallization from alcohol, m. p. 101-102°, it did not lower the melting point when mixed with the product from the dichloride of trichloro-

acetylamidophosphoric acid and sodium phenolate. The yield of the di-p-chlorodiphenyl ester of trichloroacetylamidophosphoric acid was 72.5%, m. p. 132-133°, and identified by its mixed melting point. The yield of the diethyl ester of trichloroacetylamidophosphoric acid was 63.0%, m. p. 46-47°, which agrees with the literature data [3].

Diphenyl ester of trichloroacetylamidophosphoric acid. To a solution of 0.025 mole of trichloroacetylamidophosphoryl chloride (6.99 g) in 50.0 ml of benzene with vigorous stirring was rapidly added 0.05 mole of dry, finely ground sodium phenolate (5.8 g). Quite strong self-heating occurred here, the phenolate precipitate disappeared, and a slimy precipitate of sodium chloride deposited. After 5-10 minutes the mixture was heated to 70-80° in 20-30 minutes, the sodium chloride was centrifuged, and the benzene was vacuum-distilled at 6 mm and 80°. The residue was an oily liquid, which rapidly crystallized when cooled and rubbed with a glass rod. The product was washed twice with 3.0 ml portions of water, once with 1.0 ml of ether, and recrystallized from alcohol; yield 50.9% (5.0 g). The diphenyl ester of trichloroacetylamidophosphoric acid crystallizes as colorless rhombohedra, m. p. 101-102°; insoluble in water, difficultly soluble in alcohol, benzene and petroleum ether, and readily soluble in ether, acetone and carbon tetrachloride. In 50% alcohol in the presence of phenolphthalein it titrates quantitatively as a monobasic acid with caustic alkali solutions.

Found %: N 3.55. Equiv. 1.004. $C_{14}H_{11}O_4NPCl_3$. Calculated %: N 3.55. Equiv. 1.000.

The di-o-chlorodiphenyl ester of trichloroacetylamidophosphoric acid was obtained in a similar manner. Yield 60.0%. It crystallizes from alcohol as small rectangular tablets, m. p. 132-133°; insoluble in water, difficultly soluble in ether and benzene, and readily soluble in acetone and CCl_4.

Found %: N 2.90. $C_{14}H_9O_4NPCl_3$. Calculated %: N 2.88.

Di-p-nitrodiphenyl ester of trichloroacetylamidophosphoric acid. A mixture of 0.2 mole of trichlorophosphazotrichloroacetyl (5.96 g), 100.0 ml of benzene and 0.602 mole of dry, finely ground sodium p-nitrophenolate (9.7 g) was boiled under reflux until the red color of the phenolate had completely disappeared, which required about 5 hours. The reaction mixture after cooling was shaken with 150.0 ml of water. The resulting precipitate was separated, washed three times with 5.0 ml portions of water, once with 2.0 ml of ether, dried, and recrystallized from benzene. Yield 84.7% (8.2 g). The di-p-nitrodiphenyl ester of trichloroacetylamidophosphoric acid crystallizes as rhombic colorless plates, m. p. 164-166°, readily soluble in acetone, more difficultly soluble in ether, difficultly soluble in alcohol, benzene, petroleum ether and carbon tetrachloride, and insoluble in water. It titrates as a monobasic acid in the presence of phenolphthalein.

Found %: N 8.47. Equiv. 0.990. $C_{14}H_9O_6N_3PCl_3$. Calculated %: N 8.66. Equiv. 1.000.

The di-o-nitrodiphenyl ester of trichloroacetylamidophosphoric acid was obtained in a similar manner. Light-yellow prisms, m. p. 175-177°; yield 41.8% (4.05 g); its solubility the same as the para-derivative.

Found %: N 8.62. Equiv. 1.010. $C_{14}H_9O_6N_3PCl_3$. Calculated %: N 8.66. Equiv. 1.000.

The trichloroacetylamidophosphoryl chloride reacts with great difficulty with nitrophenolates. After boiling for 10-15 hours in benzene solution the yields of the dinitro esters are only 5-6%.

Diphenyl ester of the N-phosphoric acid of trichloroiminoacetyl chloride. A mixture of 0.01 mole of the diphenyl ester of trichloroacetylamidophosphoric acid (3.94 g) and 0.01 mole of phosphorus pentachloride (2.1 g) was heated in an oil bath at 100-120°. The evolution of hydrogen chloride ceased after 50 minutes. The phosphorus oxychloride was vacuum-distilled at 60-70° and 5 mm. The residue contained the diphenyl ester of the N-phosphoric acid of trichloroiminoacetyl chloride, being a colorless mobile liquid, hydrolyzing with extraordinary ease under the influence of atmospheric moisture; yield 100.0% (4.13 g).

Found: acid equiv. after hydrolysis 1.92 (aq.), 2.06 (alk.). $C_{14}H_{10}O_3NPCl_4$. Calculated: equiv. after hydrolysis 2.00.

The substance was identified by treating it with water to give the diphenyl ester of trichloroacetylamidophosphoric acid. A mixture of 0.0072 mole of the substance (2.99 g) and 3.0 ml of water was shaken vigorously, the liquid chloride was immediately converted to the crystalline diphenyl ester of trichloroacetylamidophosphoric acid, which was separated, washed 3 times with 2.0 ml portions of water, and dried. Yield 95.0% (2.84 g), m. p. 100-101°; the substance was identified by its mixed melting point.

SUMMARY

It was shown that the isomeric trichlorophosphazotrichloroacetyl and N-phosphoryl chloride of trichloroiminoacetyl chloride give two series of esters when treated with alcoholates and arylates, and specifically: the trialkoxy(aroxy) phosphazotrichloroacetyls and the triesters of the N-phosphoric acid of trichloroiminoacetic acid. The chemical properties of these esters support the validity of the earlier assumed structure for the reaction products of phosphorus pentachloride with the amides of carboxylic acids, as being trichlorophosphazoacyls, and not the N-phosphoryl chlorides of iminoacyl chlorides.

LITERATURE CITED

[1] A. V. Kirsanov and G. I. Derkach, J. Gen. Chem. 26, 2009 (1956).

[2] A. V. Kirsanov and V. I. Shevchenko, J. Gen. Chem. 24, 474, 882, 1980 (1954) (T. p. 483, 879, 1949).*

[3] W. Steinkopf, Ber. 41, 3571 (1908).

[4] A. V. Kirsanov, J. Gen. Chem. 22, 81 (1952) (T. p. 93);* A. V. Kirsanov and R. G. Makitra, J. Gen. Chem. 26, 905 (1956) (T. p. 1029).*

[5] A. V. Kirsanov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 646 (T. p. 551).*

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PREPARATION OF 2-NITROMETHYLQUINOLINE AND ITS DERIVATIVES

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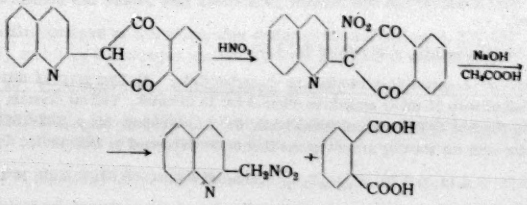
In the nature of a preliminary communication one of us [1] had described a method for the preparation of the previously unknown 2-nitromethylquinoline by the scheme:



In this paper we present complete and accurate data for the synthesis of this compound and some of its derivatives.

In principle the nitration of quinophthalone fails to differ from the method given for the earlier described [2, 3] phenyl-, naphthyl- and other 2-aryl-1,3-indandiones. The corresponding 2-nitro-2-(2-quinolyl)-1,3-indandione was obtained in excellent yield.

However, in contrast to them, the isomerization of the nitrodiketone to the corresponding esters of α-nitro-α-(2-quinolyl)-acetophenone-o-carboxylic acid proceeds not only under the influence of sodium alcoholates, but also by simple boiling of the substance in alcohol; the role of the base, catalyzing the solvolysis of the carbon-carbon bond of the indan ring, is fulfilled by the substance itself, containing the quinoline nucleus.

In this way we obtained the methyl and ethyl esters in respective yields of 75 and 83%, based on starting quinophthalone.

2-Nitromethylquinoline was obtained by the reaction of freshly prepared nitrodiketone with alkali. When treated with 10% aqueous sodium hydroxide solution the substance went into solution, imparting a dark-red color, and after acidification with acetic acid the 2-nitromethylquinoline was obtained as a precipitate. The yield of pure product was 54%, based on quinophthalone. The substance when treated with 80% sulfuric acid, and also when oxidized, gives quinaldic acid, which unequivocally proves its structure as being a primary nitro compound.

EXPERIMENTAL

1. Nitration of quinophthalone. Ten grams of technical quinophthalone (m. p. 210-215°) was covered with 75 ml of nitric acid (d 1.44). When shaken, the substance dissolved with a red color and nitrogen oxides were evolved. Usually several seconds are required for solution, after which the mixture was poured into water. The light-colored precipitate was rapidly separated (for it becomes very dark on standing), washed with water, and

dried. Weight 9.8 g, m. p. 145-147° (with decomp.). Recrystallization from 45 ml of benzene gave 2.7 g of pure nitro product as cream-colored needles. M. p. 151-152° (with decomp.). It turns red when stored.

Found %: C 68.23; H 3.36; N 8.86. M 316.5 (ebullioscopically). $C_{18}H_{10}O_4N_2$. Calculated %: C 67.92; H 3.14; N 8.81. M 318.

2. Methyl α-nitro-α-(2-quinolyl)-acetophenone-o-carboxylate. a) A mixture of 1 g of nitroquinophthalone with m. p. 151-152° and 15 ml of methanol was boiled for 15 minutes. A yellow crystalline precipitate was obtained on cooling (appears as needles under the microscope). M. p. 181-182° (with decomp.). The yield of the methyl α-nitro-α-(2-quinolyl)-acetophenone-o-carboxylate was 0.82 g (75 %).

Found %: C 65.04; H 3.97; N 7.87. $C_{19}H_{14}O_5N_2$. Calculated %: C 65.14; H 4.00; N 8.00.

b) Technical quinophthalone (24 g) was dissolved with vigorous shaking in a mixture of 100 ml of 98% acetic acid and 90 ml of nitric acid (d 1.38). The phthalone dissolved completely after shaking for 10 minutes; here nitrogen oxides were evolved. The mixture was diluted with water, suction-filtered, and in the crude state was treated with 3% sodium methylate in methanol. The solution was strongly diluted with water and acidified with dilute sulfuric acid. The yellow precipitate was separated and boiled in ethyl alcohol. Yield 10 g. M. p. 181-182° with swelling.

Found %: N 8.06. $C_{19}H_{14}O_5N_2$. Calculated %: 8.00.

3. Ethyl α-nitro-α-(2-quinolyl)-acetophenone-o-carboxylate. a) One gram of nitroquinophthalone with m. p. 151-152° was boiled with 15 ml of anhydrous ethanol for 15 minutes. Yellow crystals of the ethyl ester deposited after cooling (appear as thin slanted plates under the microscope). M. p. 152-153°. Yield 0.95 g (83%). Its mixed melting point with the starting nitrodiketone is strongly depressed to 125-127°.

Found %: C 66.09; H 4.44; N 7.90. $C_{20}H_{16}O_5N_2$. Calculated %: C 65.93; H 4.39; N 7.69.

b) Technical quinophthalone (60 g) (m. p. 210-215°) was gradually added to a mixture of 200 ml of 98% acetic acid and 200 ml of nitric acid (d 1.50), with cooling of the reaction mixture with water. The mixture was allowed to stand for 10 minutes after solution had been achieved; then it was poured into 2 liters of cold water; the moist large-grained precipitate was washed with hot alcohol and then dried. Weight 50 g. Recrystallization from 350 ml of ethanol gave 36 g of the ethyl ester with m. p. 151-152°. Its mixed melting point with the product obtained in "a" was not depressed.

Found %: N 7.76. $C_{20}H_{16}O_5N_2$. Calculated %: N 7.69.

4. Preparation of 2-nitromethylquinoline. a) Sixty grams of technical quinophthalone was dissolved in a mixture of 300 ml of 98% acetic acid and 100 ml of nitric acid (d 1.48). After shaking for 10 minutes the mixture was poured into cold water, the precipitate was separated, and in the moist state was stirred with 400 ml of 10% aqueous sodium hydroxide solution. On heating to 60° the substance nearly all dissolved with a dark-red color. The solution was filtered, diluted with water, and acidified with acetic acid. Yellow flocs of the nitro compound deposited, going first to a liquid, and then to a solid product. The yellow powder was separated, m. p. 115-116°, weight 38 g. Recrystallization from alcohol gave 22 g of coarse brown crystals with a violet luster. M. p. 121-122°. Yield 54%, based on starting quinophthalone. Further purification failed to change the melting point.

Found %: C 63.83; H 4.52; N 14.86. M 184 (ebullioscopically). $C_{10}H_8O_2N_2$. Calculated %: C 63.83; H 4.31; N 14.89. M 188.

The acetic acid filtrate, remaining after removal of the 2-nitromethylquinoline, was treated with a freshly prepared aqueous solution of lead acetate. After long standing a heavy precipitate of lead phthalate deposited, which was separated, washed well with water, dried, and treated with concentrated sulfuric acid. The obtained precipitate of phthalic acid was extracted with ether. Evaporation of the ether solution gave the phthalic acid as a white crystalline powder. M. p. 200-202°. The substance sublimes completely as phthalic anhydride with m. p. 130°. Its mixture with the authentic preparation melts without depression.

b) Twenty grams of quinophthalone was treated with 200 ml of nitric acid (d 1.44), and then as described in "a". The moist nitro derivative was dissolved in 200 ml of 10% sodium hydroxide, diluted with an equal volume

of water, and acidified with dilute acetic acid. The yield of substance was 13.6 g, which after recrystallization from 150 ml of alcohol gave 5.05 g of 2-nitromethylquinoline with m. p. 121-122°.

Found %: N 15.12. $C_{10}H_8O_2N_2$. Calculated %: N 14.89.

The substance is readily soluble in many organic solvents – alcohol, acetic acid, benzene, xylene, acetone methyl alcohol, chloroform, carbon tetrachloride. Difficultly soluble in diethyl ether and water. One gram of the substance dissolves in 600 ml of water at 20°, i. e. its saturated solution contains 1.66 g of substance per liter.

The substance is readily soluble in both concentrated and dilute acids and alkalies. It gives a picrate with picric acid, and it forms addition products with some inorganic salts.

5. Oxidation of 2-nitromethylquinoline. A mixture of 5 g of finely ground 2-nitromethylquinoline and 10 g of sodium bichromate was covered with 50 ml of glacial acetic acid. The substance rapidly went into solution, and the mixture showed self-heating to a temperature of approximately 70°. After boiling for 10 minutes the green solution was poured into water, the insoluble inorganic portion was removed by filtration, and the filtrate was treated with ether. The ether extract was dried over sodium sulfate, and the ether was distilled off.

The semiliquid residue was washed with acetic acid, filtered, and recrystallized from the same solvent.

The white crystals, obtained as thin plates after drying in the air, had m. p. 136-137°, which agrees with the literature data [4], and from the nitrogen analysis were the dihydrate of quinaldic acid.

Found %: N 6.67. $C_{10}H_7O_2N \cdot 2H_2O$. Calculated %: N 6.70.

After drying in a drying oven at 110° for 1 hour the substance was converted to the anhydrous product with m. p. 155-156°, which also agrees with the literature data.

Found %: N 8.35. $C_{10}H_7O_2N$. Calculated %: N 8.09.

An aqueous solution of the substance gives a yellow-red color with iron sulfate, which is characteristic for quinaldic acid.

6. Action of sulfuric acid on 2-nitromethylquinoline. Five grams of the nitro derivative was ground and covered with 50 ml of 80% sulfuric acid. The suspension was cautiously heated at 120-130° for approximately 1 hour with frequent shaking.

The nitro compound completely dissolved during the heating process with the formation of a brown-colored solution. The mixture after cooling was poured into water, the water solution was treated with ether, the ether extract was dried over sodium sulfate, and the ether was distilled off.

Further treatment was the same as described in Section 5. Here we obtained long white plates of quinaldic acid dihydrate with m. p. 135-136°. After drying at 110°, m. p. 155-156°. Its mixture with the substance obtained in Section 5 melts without depression.

Found %: N 8.23. $C_{10}H_7O_2N$. Calculated %: N 8.09.

7. 6-Methyl-2-nitromethylquinoline. 6-Methylquinophthalone (6.5 g) was treated with 45 ml of nitric acid (d 1.43), the same as already described above. After washing with water the moist nitration product was dissolved under slight warming in 60 ml of 10% sodium hydroxide solution, diluted with an equal volume of water, and then filtered. The orange filtrate was acidified with acetic acid, the yellow precipitate separated, and washed. The nitro derivative (3.1 g), as shown by nitrogen analysis, required further purification. Recrystallization from alcohol gave 2.2 g (48% based on starting phthalone) glistening golden-yellow plates with m.p. 158-159°.

Found %: C 65.51; H 4.96; N 13.56. M 205.4 (ebullioscopically). $C_{11}H_{10}O_2N_2$. Calculated %: C 65.34; H 4.45; N 13.87. M 202.0

8. Preparation of 6,8-dimethyl-2-nitromethylquinoline. Six grams of 6,8-dimethylquinophthalone was treated with 35 ml of nitric acid (d 1.43), as indicated above. The moist nitration product was dissolved under slight warming in 70 ml of 10% aqueous sodium hydroxide solution, the filtrate made acid with dilute acetic acid, the yellow precipitate separated, and then dried at room temperature for four days. Weight 4.3 g, m. p. ~ 154° (with decomp.). Recrystallization of the substance from alcohol gave two fractions of crystals. The 1st fraction weighed 0.3 g and had m. p. 172°. It was not studied further; the 2nd fraction weighed 1.5 g and melted at 185°.

Long slender light-brown platelets, based on the analysis data being the desired 6,8-dimethyl-2-nitromethylquinoline. The yield of the substance was 35%, based on the starting phthalone.

Found %: C 66.42; H 5.56; N 12.86. $C_{12}H_{12}O_2N_2$. Calculated %: C 66.65; H 5.55; N 12.96.

SUMMARY

A simple and convenient method was developed for obtaining 2-nitromethylquinoline and its derivatives.

LITERATURE CITED

[1] L. P. Zalukaev, Bull. Acad. Sci. Latvian SSR 1953, 11, 111.

[2] L. P. Zalukaev, Bull. Acad. Sci. Latvian SSR 1954, 3, 101.

[3] L. P. Zalukaev and E. V. Vanag, J. Gen. Chem. 26, 607 (1956) (T. p. 657). *

[4] O. Doebner and W. Miller, Ber. 16, 2472 (1883).

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*T. p. = C. B. Translation pagination.

CHLORIDES AND ESTERS OF URETHANPHOSPHORIC ACIDS

A. V. Kirsanov and I. N. Zhmurova

The recently synthesized chloride of isocyanatophosphoric acid, Cl_2PONCO (I), is extremely reactive [1] and can serve as the starting product for the preparation of a large number of phosphoric acid derivatives. Thus, for example, the isocyanatophosphoryl chloride can add to the −NCO group in alcohols and phenols, forming the chlorides of the urethanphosphoric acids, $Cl_2PONHCOOR$ (II), where R = Alk or Ar. With methyl, ethyl and isopropyl alcohols the isocyanatophosphoryl chloride reacts very vigorously, with strong self-heating. The reaction is best run in petroleum ether with ice water cooling. The reaction products, insoluble in petroleum ether, first deposit as oils, which then crystallize. The chlorides of the alkylurethanphosphoric acids are very reactive, being readily hydrolyzed by atmospheric moisture, for which reason their purification and recrystallization are difficult. The reaction of isocyanatophosphoryl chloride with n-butyl, isobutyl and isoamyl alcohols yields liquids that are soluble in petroleum ether and have a very sharp, disagreeable odor. They decompose when vacuum-distilled. Their isolation and purification could not be accomplished.

The reaction with phenol is much less vigorous. The reaction proceeds slowly and without self-heating. The introduction of electronegative substituents into the phenol molecule leads to further retardation of the reaction. The o- and p-nitrophenols are completely unreactive toward isocyanatophosphoryl chloride. Electropositive substituents accelerate the reaction: p-methoxyphenol reacts more vigorously than does phenol.

The aryl derivatives are much more stable than the alkyl. Thus, the chloride of methylurethanphosphoric acid is decomposed by cold water in 2-3 minutes, while the corresponding phenyl derivative is hydrolyzed in approximately 30 minutes. The chloro- and bromophenyl derivatives are hydrolyzed very slowly by cold water; at 70-80° the hydrolysis goes in several minutes.

In the presence of phenolphthalein the chlorides of the urethanphosphoric acids titrate as 4 equivalents with sodium hydroxide solution.

The yields, melting points and analysis results of the obtained chlorides of general formula (II) are presented in Table 1.

TABLE 1

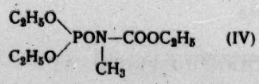
Chlorides of Urethanphosphoric Acids of Type $Cl_2PONHCOOR$

Expt. Nos.	R	Melting point	Yield (in %)	Empirical formula	Analysis results: chlorine determination (in %) found	chlorine determination (in %) calculated	acid equivalent when hydrolyzed (in %) found	acid equivalent when hydrolyzed (in %) calculated
1	CH_3	47—50°	70	$C_2H_4O_3NPCl_2$	35.87, 35.94	37.00	3.89, 3.88	4.00
2	C_2H_5	20—25	71	$C_3H_6O_3NPCl_2$	—	—	3.69, 4.20	4.00
3	iso-C_3H_7	74—78 (with decompn.)	50	$C_4H_8O_3NPCl_2$	—	—	3.96, 4.01	4.00
4	C_6H_5	102—104 (with decompn.)	77	$C_7H_6O_3NPCl_2$	28.22, 28.10	27.95	—	—
5	C_6H_4Cl-o	100—102	69	$C_7H_5O_3NPCl_3$	24.35, 24.35	24.61 •	—	—
6	C_6H_4Cl-	115—117	55	$C_7H_5O_3NPCl_3$	24.85, 24.90	24.61 •	—	—
7	C_6H_4Br-	124—126	78	$C_7H_5O_3NPCl_2Br$	20.89, 20.98	21.32	—	—
8	$C_6H_4OCH_3$-	90— 96	84	$C_8H_8O_3NPCl_2$	—	—	4.03, 4.04	4.00

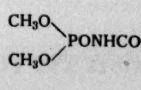
• Hydrolyzable chlorine.

When reacted with alcoholates and phenolates the chlorides of the urethanphosphoric acids form urethanphosphoric acid esters of general formula $(RO)_2PONHCOOR'$ (III), where R and R' = Alk or Ar.

The urethanphosphoric acids and their derivatives have not been known until recently. Only one member of this class of compounds had been obtained – the diethyl ester of N-methylethylurethanphosphoric acid (IV) [2].



(IV)



(V)

Only the chlorides of the alkylurethanphosphoric acids were used in the present study to obtain the esters.

The reaction of sodium methylate with the chloride of methylurethanphosphoric acid gave the dimethyl ester of methylurethanphosphoric acid (V).

We were unable to synthesize the alkyl homologs of compound (V). The reaction of isocyanatophosphoryl chloride with isopropyl, n-butyl and isobutyl alcohols, and then with the corresponding alcoholates, gave the trialkyl phosphates as the main reaction products. Evidently, in the reaction of ethyl alcohol and sodium ethylate a mixture of triethyl phosphate and diethyl ethylurethanphosphate is formed. We were unable to separate the mixture of these two substances.

When reacted with phenolates the chlorides of the alkylurethanphosphoric acids form the diaryl esters of the alkylurethanphosphoric acids. The smoothest reaction is obtained with phenol itself. The substituted phenolates, both with electropositive (o- and p-cresolate, p-methoxyphenolate) and with electronegative substituents (o-chlorophenolate and p-bromophenolate), react less vigorously, the esters are formed in low yields, and are contaminated by tarry impurities. The o- and p-nitrophenolates are completely unreactive and fail to form the esters. Very small amounts of trinitrotriphenyl phosphates are formed under the reaction conditions.

The yields and melting points of the compounds of general formula (III) are presented in Table 2.

TABLE 2

Esters of Urethanphosphoric Acids of Type $(RO)_2PONHCOOR'$

Expt. Nos.		R'	Melting points	Yield (in % based on $ClPONCC_6$)	Empirical formula	Analysis results (in %) found		calculated	
1	CH_3 . . .	CH_3	63— 65	50—54	$C_4H_{10}O_5NP$	N	7.36, 7.46	N	7.65
2	C_2H_5 . . .	CH_3	109—111	43	$C_{14}H_{14}O_5NP$	N	4.60, 4.50	N	4.54
3	C_6H_5 . . .	C_2H_5	94— 96 (with decompn.)	36 *	$C_{15}H_{16}O_5NP$	N	4.36, 4.33	N	4.35
4	C_6H_5 . . .	iso-C_3H_7	79— 81 (with decompn.)	31	$C_{16}H_{18}O_5NP$	N	4.18, 4.26	N	4.18
5	n-BrC_6H_4 .	CH_3	152—154	34	$C_{14}H_{13}O_5NBr_2P$	Br	34.03, 34.30	Br	34.19
6	n-BrC_6H_4 .	C_2H_5	98—100	19	$C_{15}H_{14}O_5NBr_2P$	Br	33.75, 33.79	Br	33.40
7	n-BrC_6H_4 .	iso-C_3H_7	114—116	18 *	$C_{16}H_{16}O_5NBr_2P$	Br	32.40, 32.60	Br	32.45
8	o-ClC_6H_4 .	CH_3	116—118	25	$C_{14}H_{13}O_5NPCl_2$	Cl	18.27, 18.28	Cl	18.85
9	o-ClC_6H_4 .	C_2H_5	78— 80	19	$C_{16}H_{14}O_5NPCl_2$	Cl	18.31, 18.03	Cl	18.20
10	n-$CH_3C_6H_4$	CH_3	149—151	20	$C_{15}H_{18}O_5NP$	N	4.18, 4.14	N	4.18
11	n-$CH_3C_6H_4$	C_2H_5	100—101	10	$C_{17}H_{20}O_5NP$	N	4.00, 4.08	N	4.01
12	o-$CH_3C_6H_4$	CH_3	135—136	14	$C_{16}H_{18}O_5NP$	N	4.23, 4.24	N	4.18
13	n-$CH_3OC_6H_4$	CH_3	103—105	33	$C_{16}H_{18}O_7NP$	N	3.72, 3.74	N	3.81

* As the sodium salt.

Esters 1-13 represent colorless crystalline compounds, soluble in alcohol and benzene, and insoluble in petroleum ether. Ester 1 is also soluble in water. Compounds 2-13 dissolve in 0.5-1% aqueous alkali solution with the formation of sodium salts.

The reaction for the preparation of esters 2-4 can be run with either two or three moles of the phenolate. The sodium salt is formed in the latter case. The amount of phenolate fails to essentially influence the yield. In the case of the substituted phenolates an excess of the phenolate exerts a negative influence.

EXPERIMENTAL

Chlorides of Urethanphosphoric Acids

Chlorides of alkylurethanphosphoric acids. To a solution of 0.1 mole of isocyanatophosphoryl chloride was gradually added with ice-cooling 0.1 mole of the corresponding alcohol. The chloride of the alkylurethanphosphoric acid, initially depositing as an oil, crystallized when cooled in an ice-salt mixture and rubbed with a glass rod. The crystals were filtered, washed with petroleum ether, and dried in a vacuum-desiccator. Compounds 1-3 were obtained in this manner (Table 1).

Chlorides of arylurethanphosphoric acids. To a solution of 0.025 mole of the proper phenol in the minimum amount of petroleum ether (30 ml for phenol, 10 ml for the o- and p-nitrophenols) was added 0.025 mole of isocyanatophosphoryl chloride. After several hours the precipitate of arylurethanphosphoric acid was filtered and dried in a vacuum-desiccator. The reaction with the p-bromo- and p-methoxyphenols, both insoluble in petroleum ether, was run in ether (3-5 ml). We obtained compounds 4-8 in this manner (Table 1).

Esters of Urethanphosphoric acids

Dimethyl ester of methylurethanphosphoric acid (1). To 8 g (0.05 mole) of isocyanatophosphoryl chloride was gradually added with ice water cooling a solution of 1.6 g of methyl alcohol in 20 ml of benzene, and then a solution of the sodium alcoholate, obtained by dissolving 2.3 g of metallic sodium in 50 ml of absolute methyl alcohol. The alcoholate was added at a temperature of 1-2° (inside the reactor). A higher temperature results in a considerably lower yield of the ester. The sodium chloride precipitate was filtered, the benzene and excess alcohol removed by distillation, the residue treated with 150 ml of dry benzene, the undissolved tarry impurities removed by filtration, the benzene distilled off, the residue dissolved in a small amount of benzene, and the solution allowed to stand overnight in the cold. The dimethyl ester of methylurethanphosphoric acid deposited as a colorless crystalline precipitate. Yield 4.4 g.

Diphenyl ester of methylurethanphosphoric acid (2). To a solution of 8 g of isocyanatophosphoryl chloride in 25 ml of benzene was added with ice cooling 1.6 g of methyl alcohol. To the solution of methylurethanphosphoryl chloride obtained in this manner was gradually added 18 g of sodium phenolate. The addition of the phenolate was made at room temperature, and the reaction mixture was cooled externally by ice water when reaction was slightly too violent. On conclusion of reaction the mixture was treated with water and here the sodium salt of the ester, formed as a reaction result, went into the water layer. To completely extract the salt the benzene layer was washed several times with dilute alkali. The aqueous alkaline extracts were combined and acidified with dilute hydrochloric acid. The ester deposited as an oil, which soon crystallized. Yield 6.7 g. Colorless prisms (from equal volumes of benzene and petroleum ether).

Diphenyl ester of ethylurethanphosphoric acid (3). Obtained in the same manner as the preceding. On conclusion of reaction the mixture was treated with water. In contrast to the salt of ester (2), the sodium salt of ester (3) is difficultly soluble in water and fails to go into the water layer. After separating from the water, the benzene layer was shaken with 20 ml of 40% alkali; here the sodium salt of the ester was obtained as a precipitate. The precipitate was filtered. A second treatment of the benzene layer with alkali gave an additional amount of the salt. From 6.9 g of isocyanatophosphoryl chloride was obtained 5.3 g of the ester sodium salt. Treatment of an aqueous suspension of the salt with dilute hydrochloric acid gave 3.6 g of the ester. The substance was purified by its precipitation from benzene solution with petroleum ether.

The diphenyl ester of isopropylurethanphosphoric acid (4) was obtained in a manner similar to the preceding. On conclusion of reaction the reaction mixture was treated with water, and the water layer was separated. As in the previous experiment, the salt of ester (4) fails to go into the water layer. After a day the sodium salt of the ester crystallized from the benzene layer. The salt was filtered, air-dried, suspended in water, and decomposed with hydrochloric acid. The ester deposited as an oil, which soon crystallized. The precipitate was filtered, dried, and recrystallized from petroleum ether.

Di-p-bromodiphenyl ester of methylurethanphosphoric acid (5). To a solution of 8.65 g of p-bromophenol [3] in 50 ml of benzene was added 1.15 g of comminuted metallic sodium. The mixture was boiled under reflux until all of the sodium had dissolved (about 6 hours). To the suspension of sodium bromophenolate was added a benzene solution of methylurethanphosphoryl chloride, obtained, as usual, from 4 g of isocyanatophosphoryl chloride and 0.8 g of methyl alcohol. The reaction went with moderate self-heating. The reaction mass was shaken with water, the benzene layer was separated, the benzene distilled off, and the residual oil rubbed in the cold with alcohol, after which it crystallized. The crystals were filtered and washed with cold alcohol. The substance was purified by recrystallization from alcohol.

The di-p-bromodiphenyl ester of ethylurethanphosphoric acid (6) was obtained in the same manner as the preceding. On conclusion of reaction the mixture was treated with water, the water layer was separated, and the benzene layer was treated 3 times with 20 ml portions of 5% sodium hydroxide. Acidification of the alkaline extract gave an oil, which could not be made to crystallize. The benzene layer was washed twice with water. Acidification of the wash waters gave an oil, which soon crystallized. The crystals were filtered and washed with cold alcohol, after which the product was recrystallized from a small volume of alcohol.

Di-p-bromodiphenyl ester of isopropylurethanphosphoric acid (7). The reaction was run the same as the preceding. On conclusion of reaction the mixture was treated with water, the water layer was separated, and the benzene layer was treated with 40% alkali. The aqueous alkaline extract was separated, diluted with water, and acidified with dilute hydrochloric acid. Here an oil deposited, which could not be made to crystallize. White flocs of the sodium salt of the ester deposited from the benzene layer after two days. The salt precipitate was filtered, dried, and treated in the cold with concentrated hydrochloric acid. The resulting viscid mass was separated from the acid by decantation and washed with water. The substance crystallized after treatment in the cold with a small amount of alcohol. The precipitate of the ester was filtered and recrystallized from alcohol.

Di-o-chlorodiphenyl ester of methylurethanphosphoric acid (8). To a benzene suspension of the o-chlorophenolate, obtained in the same manner as the p-bromophenolate from 0.05 mole ofo-chlorophenol and 0.05 mole of metallic sodium, was added a freshly prepared benzene solution of 0.025 mole of methylurethanphosphoryl chloride. The reaction went with moderate self-heating. To complete the reaction the mixture was heated at the boil for 5 minutes. The sodium chloride was removed with water, and the benzene layer was treated 3 times with 25 ml portions of 5% sodium hydroxide. The aqueous alkaline extracts were combined and acidified. The resulting oil was separated from the water by decantation and poured into a Petri dish. The oil crystallized after 3 days. The substance was purified by its precipitation from hot benzene solution with petroleum ether.

The di-o-chlorodiphenyl ester of ethylurethanphosphoric acid (9) was obtained in the same manner as the preceding. The reaction product was isolated as an oil, which partially crystallized after a day. The crystals were pressed on porous plate and purified by recrystallization from petroleum ether.

Di-p-cresyl ester of methylurethanphosphoric acid (10). To a solution of 5.4 g of p-cresol in 50 ml of benzene was added 1.15 g of sodium. The mixture was boiled for 6 hours. To the cresolate suspension was added a freshly prepared solution of 0.025 mole of methylurethanphosphoryl chloride. The reaction went with moderate self-heating. The sodium chloride was extracted with water. The benzene layer was treated 3 times with 20 ml portions of 5% sodium hydroxide. The aqueous alkaline extracts were combined and acidified with hydrochloric acid. Here an oil deposited, which crystallized when the reaction mixture was shaken with 20 ml of petroleum ether. The crystals were filtered and washed with petroleum ether. The substance was purified by its precipitation from benzene solution with petroleum ether.

The di-p-cresyl ester of ethylurethanphosphoric acid (11) was obtained in the same manner as the preceding. After running the reaction the sodium chloride was removed with water, and the benzene layer was treated with 40% sodium hydroxide. Acidification of the aqueous alkali extract gave an oil, which could not be made to crystallize. The sodium salt of the ester was extracted by subsequent washing of the benzene layer with water and dilute alkali. Acidification of the alkaline solution gave the crystalline ester. The product was purified in the same manner as the preceding.

The di-o-cresyl ester of methylurethanphosphoric acid (12) was obtained and purified in the same manner as the preceding.

Di-p-methoxydiphenyl ester of methylurethanphosphoric acid (13). To a solution of 1.15 g of sodium in 30 ml of methyl alcohol was added 6.2 g of hydroquinone monomethyl ester. The methyl alcohol was removed by vacuum-distillation. To the dry p-methoxyphenolate was added 50 ml of benzene, and then a freshly prepared benzene solution of 0.025 mole of methylurethanphosphoryl chloride. The mixture was heated on the water bath for 10 minutes. The sodium chloride was removed with water, and the benzene layer was treated 3 times with 25 ml portions of 5% sodium hydroxide. Acidification of the aqueous alkali extracts gave an oil, which solidified in an hour. The substance was purified by its precipitation from benzene solution with petroleum ether.

The yields, melting points and analysis data for esters 1-13 are presented in Table 2.

Reaction of the chlorides of methyl- and ethylurethanphosphoric acids with the o- and p-nitrophenolates. To a solution, obtained in the usual manner, of 0.025 mole of methylurethanphosphoryl chloride in 30 ml of benzene was added 0.05 mole of the o-nitrophenolate. The mixture was boiled under reflux for 10 minutes. The nitrophenolate disappeared (the color of the precipitate changed from yellow to white). The residue was a yellow oil. The oil was treated with cold methyl alcohol to give a white crystalline substance with m. p. 127-129, which agrees with the m. p. given in the literature [4] for tri-o-nitrotriphenyl phosphate. Yield 11%, based on isocyanatophosphoryl chloride. Here o-nitrophenol was also isolated. The chloride of ethylurethanphosphoric acid reacts with o-nitrophenol in a similar manner.

The reaction of the chloride of methylurethanphosphoric acid with p-nitrophenolate gave the tri-p-nitrotriphenyl phosphate. M. p. 153-154°, which agrees with the literature data [5].

SUMMARY

1. The chlorides of some alkyl- and arylurethanphosphoric acids were synthesized.

2. The chlorides of the alkyl- and arylurethanphosphoric acids were converted to the esters of alkyl- and arylurethanphosphoric acids.

LITERATURE CITED

[1] A. V. Kirsanov, J. Gen. Chem. 24, 1033 (1954) (T. p. 1031);* Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 646 (T. p. 551).*

[2] B. A. Arbuzov, P. I. Alimov and M. A. Zvereva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 1042 (T. p. 909).*

[3] W. Autenrieth and P. Muhlinghaus, Ber. 40, 747 (1907).

[4] A. Engelhardt and P. Lachimov, J. Russ. Phys.-Chem. Soc. 2, 116 (1870).

[5] M. Rapp, Ann. 224, 166 (1884).

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*T. p. = C. B. Translation pagination.

ULTRAVIOLET AND VISIBLE ABSORPTION SPECTRA OF TRIPHENYLAMINE AND ITS p-NITRO DERIVATIVES IN CONCENTRATED SULFURIC ACID. II

P. M. Bugai

W. Dilthey [1] described the oxidation of triphenylamine and the formation of blue-colored salts of the ammenium type. A. E. Chichibabin [2] mentioned that when triphenylamine is heated in strong sulfuric acid it dissolves with a blue color. An elucidation of the reason for the relationship between the color of triphenylamine and its p-nitro derivatives and their structure is the purpose of the present investigation. We made a spectrographic study of these substances in various solvents: in ethanol, in ethanol in the presence of sodium alcoholate [3], and in concentrated sulfuric acid. Here we will discuss only the study of these substances in concentrated sulfuric acid.

All of the studied p-nitro derivatives of triphenylamine were synthesized by our earlier developed method [4], and then, together with the necessary solvents, were purified to spectroscopic purity. The studies were made with a type ISP-22 spectrograph, using "Panchrome" film, sensitive to visible light.

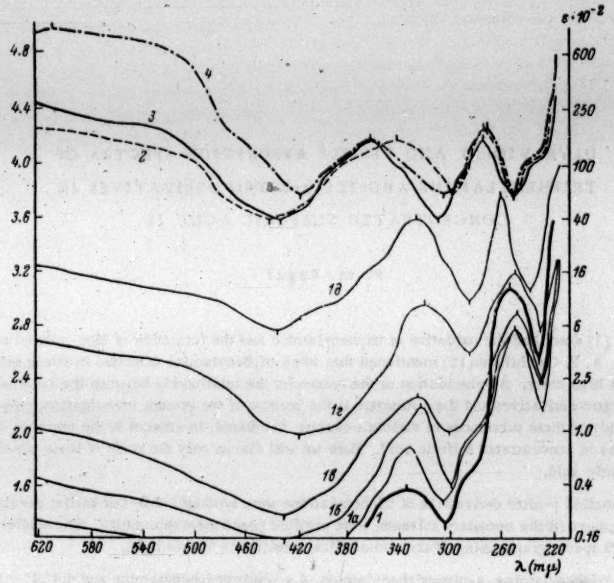
We studied triphenylamine, 4-nitrotriphenylamine, 4,4'-dinitrotriphenylamine and 4,4',4"-trinitrotriphenylamine. The absorption spectra of these substances in concentrated sulfuric acid solution are shown in the Figure, as is also the color of the substances.

In studying the color of triphenylamine we established that the color of the triphenylamine solution in concentrated sulfuric acid, in the absence of heat, after prolonged standing from 1 to 12 days constantly becomes more intense and goes to an intense blue and then to a green; the solutions are no longer transparent at a concentration of $1 \cdot 10^{-3}$ M.

Studying this characteristic of triphenylamine, we also obtained the curves for the absorption spectra of triphenylamine in concentrated sulfuric acid, beginning from the moment of dissolving it in the acid (here the solution was colorless), and then photographing it after 1, 2, 3, 7 and 12 days. In this connection the color strongly deepened and rapidly became stronger, changing from a pale blue to an intense blue and then to a green. The character of the spectral curve also changed with change in the solution color. These changes are clearly illustrated by the curves: 1, 1a, 1b, 1c, 1d and 1e (see Figure). Here we observe that the whole triphenylamine spectral curve with its absorption bands is lifted upwards; consequently the absorption intensity increases sharply due to the fact that a product of constantly greater color is formed in the reaction of triphenylamine with concentrated sulfuric acid. Here the manner in which a broad absorption band develops in the visible region can be plainly seen.

It is characteristic that the two main absorption bands (their maxima) of triphenylamine, which are found at log ϵ 1.56 and λ 334 mμ and log ϵ 3.08 and λ 254 mμ, are also retained in the curves obtained after prolonged reaction with concentrated sulfuric acid, but they change in intensity and are slightly shifted either to the right or to the left. But together with this, a third band now develops.

The results of studying the p-nitrotriphenylamines are shown in the Figure by the corresponding curves 2, 3 and 4. All of these curves each have two principal absorption maxima – one in the ultraviolet region at



1) Triphenylamine immediately after dissolving in H_2SO_4 (solution colorless), 1a) after 1 day (light-blue), 1b) after 2 days (pale-blue), 1c) after 3 days (blue), 1d) after 7 days (intensely blue), 1e) after 12 days (very intensely blue); 2) 4-nitrotriphenylamine immediately after dissolving (very intensely blue); 3) 4,4'-dinitrotriphenylamine immediately after dissolving (intensely blue); 4) 4, 4"-trinitrotriphenylamine immediately after dissolving (intensely cherry-red).

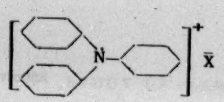
the values log ε 4.19-4.26 and λ 273-274 mμ and the other in the visible region at the values log ε 4.19 and λ 361, 360 and 342 mμ. But, in addition, there is still a third band, which extends far into the long-wave region. In this case curves 2 and 3 have only absorption minima, lying in the wavelength interval 430-440 mμ at log ε 3.60, while curve 4, besides a minimum, found at log ε 3.78 and λ 434 mμ, also has a new maximum at log ε 4.96 and λ 604 mμ.

It is important to mention here that the color of the p-nitro derivatives of triphenylamine in concentrated sulfuric acid strongly deepens and for the 4-nitrotriphenylamine goes from a yellow in alcohol solution to an intense blue, for the 4,4'-dinitrotriphenylamine it goes from a yellow to an intense blue, and for the 4,4',4"-trinitrotriphenylamine it goes from a yellow-orange to an intense red.

All of this occurs as the result of the action of sulfuric acid on these substances. The color of the triphenylamine solution after standing for 12 days in concentrated sulfuric acid becomes similar to the color of the 4-nitrotriphenylamine, and the triphenylamine curve itself now approximates in character the curve of this nitro derivative. The number of bands with absorption maxima also coincide, and they are closely similar in their wavelengths, while in its character the third, extended band with its absorption maximum in the long-wave region, copies as it were the bands of curves 2 and 3. Such closeness of the absorption bands of the colored triphenylamine solution with those of the nitro derivatives of triphenylamine, and the fact that nearly the same color is obtained for these solutions in concentrated sulfuric acid, suggest that the same type of chemical reaction is involved in the action of concentrated sulfuric acid on triphenylamine and its nitro derivatives.

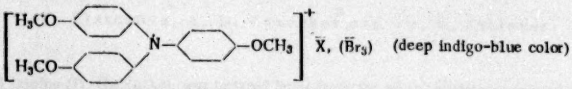
As is known [5], organic salts of the ammonium type are colorless, the same as their corresponding amines; consequently, our substances form salts of a different, ionic character.

W. Dilthey indicated [1] that a salt of the triphenylammenium type can be formed in the oxidation of triphenylamine:



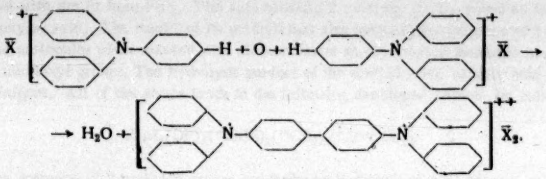
(intensely blue color)

while for the derivatives of triphenylamine H. Wieland [6] presents the following structural formula:



(deep indigo-blue color)

With further, stronger oxidation the colored triphenylammenium salt forms another salt of the bivalent tetraphenylbenzidine ion, which W. Dilthey presents in his paper [1]:



(blue color)

Proceeding from the literature data [1, 6], we can assume that possibly the oxidation of triphenylamine and its p-nitro derivatives in concentrated sulfuric acid proceeds in a manner similar to the oxidation of other substances, but that it also requires further study.

SUMMARY

1. The formation of color for triphenylamine in concentrated sulfuric acid is associated with its oxidation by the sulfuric acid and the subsequent formation of salts of the ammenium type.

2. Apparently, the origin of a deepened color for the p-nitro derivatives of triphenylamine is also the result of the formation of similar compounds, in connection with which their color is comparable to the color of the oxidized triphenylamine.

LITERATURE CITED

[1] Dilthey, J. prakt. Chem. (2) 109, 301 (1925).

[2] A. E. Chichibabin, Fundamentals of Organic Chemistry (1931), p. 473.

[3] P. M. Bugai, J. Gen. Chem. 26, 1729 (1956) (T. p. 1941).*

[4] P. M. Bugai, J. Gen. Chem. 23, 605 (1953) (T. p. 627).*

[5] R. Vitsinger, Organic Dyes (United Sci. Tech. Press, 1936), p. 20.

[6] H. Wieland, Ber. 43, 708 (1910).

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*T. p. = C. B. Translation pagination.

STUDY OF PLANT ALKALOIDS

Leontice ewersmannii BGE

IV. STRUCTURE OF THE ALKALOID TASPINE [1]

T. F. Platonova, A. D. Kuzovkov and Yu. N. Sheinker

The alkaloid taspine (I), $C_{20}H_{25}O_6N$, was isolated by us from the plant Leontice ewersmannii BGE [2]. We had already communicated [3] on a preliminary study of the alkaloid. Continuing the study, we found that oxidation of the alkaloid with chromic anhydride gives β-dimethylaminopropionic acid, which indicates that the $-CH_2CH_2N(CH_3)_2$ group is present in taspine. The Hofmann degradation of taspine methiodide results in the cleavage of trimethylamine and the salt of a nitrogen-free acid is formed. This acid (II) has the composition $C_{18}H_{22}O_8$, possesses the ability of being easily lactonized, contains one double bond, and is easily reduced when hydrogenated with the Pt from PtO_2. The acid contains 2 methoxy groups; based on analysis of the silver salt it is a dicarboxylic acid. The results of its methylation also indicate the presence of 2 carboxyls and 2 phenol hydroxyls in the molecule; when reacted with diazomethane an ester that is insoluble in alkalies is formed, which contains 6 methoxyl groups. The hydrolysis product of the methyl ester, namely acid (III) $C_{20}H_{20}O_8$, contains 2 labile hydrogens. All of the above leads to the following developed formula for acid (II):

$$C_{12}H_3(OH)_2(COOH)_2(OCH_3)_2(CH=CH_2)$$

Based on the presence of 2 carboxyl groups and 2 phenol hydroxyls in acid (II) and on the absence of these functional groups in the taspine molecule it follows that taspine contains not one lactone group, as had been postulated earlier [3], but 2 such groups. As a result, the 6 oxygen atoms found in the taspine molecule are distributed between 2 lactone groups and 2 methoxy groups. The taspine formula can then be depicted as follows:

$$C_{12}H_3(-COO)_2(OCH_3)_2[CH_2CH_2N(CH_3)_2]$$

The vinyl group in acid (III) was oxidized with potassium permanganate, and here the tricarboxylic acid (IV) of composition $C_{19}H_{18}O_{10}$ or $C_{12}H_3(OCH_3)_4(COOH)_3$ was formed. When heated this acid is easily converted to anhydride (V). The formation of the anhydride, in which one of the carboxyl groups remains free, is shown by comparing the infrared spectra of acid (IV) and its anhydride (V) (Fig. 1). Two intense bands at 1835 and 1767 cm^{-1}, characteristic for anhydrides, appear in the spectrum of the anhydride; together with this the band at 1686 cm^{-1}, present in the spectrum of acid (IV), is also retained (with reduced intensity). We compared the tricarboxylic acid (IV) with the 2',3',5,6-tetramethoxydiphenyl-2,3,6'-tricarboxylic acid (or, which is the same thing, 5,6,5',6'-tetramethoxydiphenyl-2,3,3'-tricarboxylic acid) obtained by V. V. Kiselev and R. A. Konovalova [4] in the oxidation of coridine. The identity of these substances was established by determining their mixed melting point and by comparing their infrared spectra.

The fact that 2',3',5,6-tetramethoxydiphenyl-2,3,6'-tricarboxylic acid and β-dimethylaminopropionic acid are formed from taspine as the result of the indicated reactions is proof that taspine is based on the diphenyl nucleus, containing substituents in accord with the developed formula given above. The spectral study results were used to determine the position of these substituents.

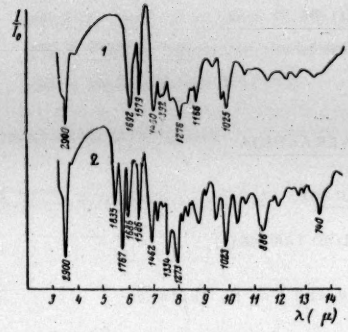


Fig. 1. Infrared absorption spectra. 1) acid (IV), 2) anhydride of the acid (V), (both in the crystalline state).

A study of the ultraviolet absorption spectrum of taspine (Fig. 2) revealed that the alkaloid possesses very intense and narrow absorption bands (λ_{max} 347, 332, 298, 285, 250 mμ). The presence in the spectrum of such bands in the long-wave region 330-350 mμ could not be reconciled with the assumption of a simple "diphenyl" nucleus for the alkaloid, since for diphenyl derivatives intense bands are observed in the 250-280 mμ region [5]. In its character the taspine spectrum is to some degree similar to the spectra of compounds with condensed nuclei [6], and it could be reconciled only with the planar structure of such a nucleus for the molecule as could contain both a diphenyl radical and, apparently, other double bonds, found in conjugation with it.

As has previously been communicated [3], the alkaline hydrolysis of taspine easily yields taspininic acid (VI), which when heated with 5% H_2SO_4 solution is again transformed into the original taspine. The ultraviolet spectrum of taspininic acid (Fig. 2) differs sharply from the spectrum of taspine. The strong absorption in the long-wave region disappears, and the intense band is shifted from the 250 m μ region (in the spectrum of taspine) to 230 mμ, and its intensity is reduced considerably. The spectrum acquires the character of the spectra of diphenyl derivatives with substituents in all four ortho-positions [5], essentially taking the diphenyl ring out of one plane. It can be assumed that the formation of a planar condensed system for the taspine nucleus with participation of diphenyl is conditioned by the lactone groups.

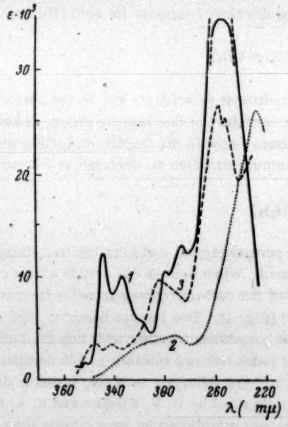


Fig. 2. Ultraviolet absorption spectra. 1) Taspine (I) (in alcohol), 2) taspininic acid (VI) (in water), 3) lactone (II) of the acid (in alcohol).

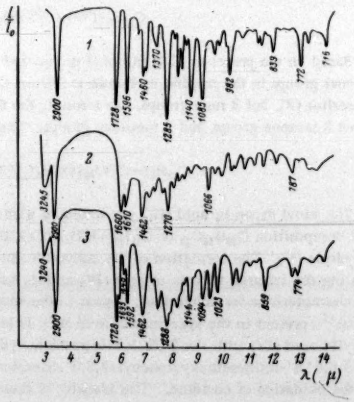
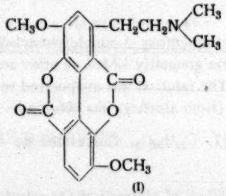


Fig. 3. Infrared absorption spectra. 1) Taspine (I), 2) taspininic acid (VI), 3) lactone (II) of the acid (all in the crystalline state).

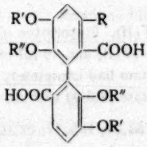
An intense carbonyl band at 1728 cm^{-1} is contained in the infrared spectrum of taspine (Fig. 3). The presence of only one such carbonyl band shows that both of the lactone groups in taspine are the same in their character and position in the molecule, and that both of them are δ-lactone groups. A band at 1770-1780 cm^{-1} is characteristic for γ-lactones, and one at about 1740 cm^{-1} for aliphatic δ-lactones; the observed reduction to 1728 cm^{-1} is conditioned by conjugation with the aromatic ring [7]. Both O–H and N–H bonds are absent in the spectrum, while bands, characteristic for aromatic rings (1596 cm^{-1}), the grouping C–O–C (1285, 1140, 1085 cm^{-1}), and the CH_2- and CH_3- groups (1460 and 1370 cm^{-1}), are present [7]. To refer a number of other bands to the vibrations of sundry other groups proved difficult. The infrared spectrum of taspininic acid (Fig. 3) shows no band for the C=O of the lactone group, but does reveal a band at 1660 cm^{-1}, characteristic for the carbonyl groups of acids, and a band at 3245 cm^{-1}, corresponding to the presence of hydroxyl groups.

The infrared spectrum of the lactone obtained from acid (II) (Fig. 3) shows a distinct band at 1728 cm^{-1} (lactone group), a very close band, merging with the former, at 1700-1695 cm^{-1} (acidic carbonyl group), a band of low intensity at 1640 cm^{-1} (the C=C double bond), and finally, a band in the 3240 cm^{-1} region, characteristic for hydroxyl groups. From this it can be concluded that apparently only one lactone group is formed in the lactone, while at the same time the second lactone group fails to cyclize under these conditions.

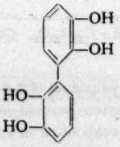
A study of the ultraviolet spectrum of the lactone (Fig. 2) leads to the same conclusion. This study shows, in comparison to taspine, that in the lactone there is some disturbance of the planar system of double bonds, although to a considerably less degree than for taspininic acid. The spectrum of the lactone shows long-wave absorption bands at 350-330 mμ (in contrast to the spectra of taspininic acid), although their intensity is greatly less than in the spectrum of taspine itself. As a result, the presented spectral data indicate that both of the lactone groups, found in the taspine molecule, are δ-lactonic, and that each of these groups is formed from a carboxyl and a hydroxyl, found in different rings. This situation, together with earlier presented cleavage results for the alkaloid, determines in a fully harmonious manner the structure of taspine (I), and of its degradation products (II-VI), described in this paper, and also of the earlier described [3] tetrahydroxydiphenyl (VII) and taspininic acid (VIII). The empirical formula of the latter should then be changed to $C_{18}H_{19}O_8N$.



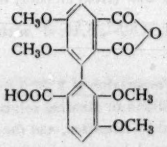
(I)



(II), (III), (IV), (VI), (VIII), (IX)



(VII)



(V)

EXPERIMENTAL

Oxidation of taspine. To a solution of 5 g of taspine in 50 ml of glacial acetic acid at 60-70° was gradually added CrO_3 until a nonfading brown color was obtained. After 6 hours the solution was filtered and evaporated

in vacuo to dryness. The residue was dissolved in dilute sulfuric acid, and the excess CrO_3 was reduced by the addition of $NaHSO_3$. The $Cr(OH)_3$ was precipitated by making the solution alkaline. The filtrate and wash water were combined, the solution was acidified with HCl, then evaporated in vacuo to dryness, and the residue was extracted with anhydrous alcohol. The solution was evaporated in vacuo to dryness, and the residue was dissolved in 5 ml of water; the reineckate [3] was obtained (0.4 g), from which the hydrochloride (0.17 g) with m. p. 183-185° (from alcohol) was prepared; its mixed melting point with the hydrochloride of β-dimethylaminn-propionic acid was 183-185°.

Hofmann degradation of taspine. Preparation of 2',6-dihydroxy-3',5-dimethoxy-3-vinyldiphenyl-2,6'-dicarboxylic acid (II). A mixture of 28.4 g of taspine methiodide and 500 ml of a 10% NaOH solution in anhydrous alcohol was boiled for 6 hours. The evolution of trimethylamine was observed. The alcohol was evaporated in vacuo, the residue dissolved in water, the solution acidified with 20% H_2SO_4 solution under cooling, and the acid solution extracted with ethyl acetate. We obtained 15.5 g of white crystalline acid (II) with m. p. 237° (from acetone). After recrystallization from water the acid melted at 171°.

Found %: C 59.62, 59.54; H 4.43, 4.54; OCH_3 17.73; H active 0.58. Equiv. 188. $C_{18}H_{16}O_8$. Calculated %: C 60.00; H 4.48; $2OCH_3$ 17.22%. 2H active 0.56. Equiv. 180.

To a solution of 0.421 g of acid (II) in 20 ml of 1 N NaOH was added a solution of 0.60 g of $AgNO_3$ in 10 ml of water. The precipitate of silver salt was washed with water and dried in a vacuum-desiccator. Yield 0.52 g.

Found %: Ag 36.85. $C_{18}H_{14}O_8Ag_2$. Calculated %: Ag 37.58.

The boiling of acid (II) with dilute HCl gave the lactone with m. p. above 360°, poorly soluble in all of the ordinary solvents.

Four grams of acid (II) was dissolved in water with the addition of NaOH solution, and then hydrogenated in the presence of skeletal nickel catalyst. The amount of hydrogen absorbed in 1 hour was 390 ml. Here we isolated 3.2 g of crystalline 3',5-dimethoxy-2',6-dihydroxy-3-ethyldiphenyl-2,6'-dicarboxylic acid (IX) with m. p. 340° (from water).

Found %: C 58.62, 58.81; H 5.23, 4.98; OCH_3 15.28. $C_{18}H_{18}O_8$. Calculated %: C 59.67; H 5.01; $2OCH_3$ 17.14.

Methylation of acid (II). Preparation of 2',3',5,6-tetramethoxy-3-vinyldiphenyl-2,6'-dicarboxylic acid (III). To a mixture of 10 g of acid (II) and 40 ml of methanol was gradually added an ether solution of diazomethane. After 12 hours the precipitate had completely dissolved. The solution was evaporated to a volume of about 15 ml. Here a crystalline precipitate (7.3 g) with m. p. 112-114° (from alcohol) was obtained.

Found %: C 63.15, 63.37; H 5.77; OCH_3 43.26, 42.17. $C_{22}H_{24}O_8$. Calculated %: C 63.45; H 5.81; $6OCH_3$ 44.72.

The methyl ester (5.7 g) was boiled for 1 hour with 60 ml of alcoholic KOH solution. Here 3.5 g of crystalline acid (III) with m. p. 208-210° (from alcohol) was obtained.

Found %: C 61.41, 61.68; H 5.34, 5.10; H active 0.48, 0.46. $C_{20}H_{20}O_8$. Calculated %: C 61.84; H 5.19; 2H active 0.52.

Oxidation of acid (III). Preparation of 2',3',5,6-tetramethoxydiphenyl-2,3,6'-tricarboxylic acid (IV). Two grams of acid (III) was oxidized in alkaline solution with potassium permanganate (3.32 g) at 91-100°. The manganese dioxide was removed by filtration, and the filtrate was evaporated in vacuo and acidified with 20% H_2SO_4; extraction with ether gave 1.1 g of acid (IV) with m. p. 120-123°, and after solidification, 233-234° [?] (from acetone); heating of the acid at 200° and 0.05 mm gave the anhydride with m. p. 233-234°.

Found %: C 58.58, 58.82; H 4.05, 4.07; OCH_3 30.49, 30.98. $C_{19}H_{16}O_9$. Calculated %: C 58.77; H 4.15; $4OCH_3$ 31.96.

The mixed melting point with the anhydride of 2',3',5,6-tetramethoxydiphenyl-2,3,6'-tricarboxylic acid (or 5,6,5',6'-tetramethoxydiphenyl-2,3,6'-tricarboxylic acid) was 234°.

The infrared absorption spectra were taken in the 2.5-14 μ region with a recording IKS-11 infrared spectrometer, using a NaCl prism. All of the substances were photographed in the crystalline state as a paste in vaseline oil. An SF-4 spectrophotometer was used to obtain the ultraviolet absorption spectra (225-400 mμ). Here the substances were studied as solutions in either water or ethyl alcohol.

SUMMARY

1. The structure of taspine (I) was established, which appears to be the di-δ-lactone of 2',6-dihydroxy-3',5-dimethoxy-3-(β-dimethylamino)ethyldiphenyl-2,6'-dicarboxylic acid.

2. The cleavage products of taspine have the following structures: 2',6-dihydroxy-3',5-dimethoxy-3-vinyldiphenyl-2,6'-dicarboxylic acid (II); 2',3',5,6-tetramethoxy-3-vinyldiphenyl-2,6'-dicarboxylic acid (III); 2',6-dihydroxy-3',5-dimethoxy-3-(β-dimethylamino) ethyldiphenyl-2,6'-dicarboxylic acid (VI); 2',3',5,6-tetrahydroxydiphenyl (2,3,2',3'-tetrahydroxydiphenyl) (VII); 2',3',5,6-tetrahydroxy-3-(β-dimethylamino) ethyldiphenyl-2,6'-dicarboxylic acid (VIII); and 2',6-dihydroxy-3',5-dimethoxy-3-ethyldiphenyl-2,6'-dicarboxylic acid (IX).

LITERATURE CITED

[1] T. F. Platonova and A. D. Kuzovkov, J. Gen. Chem. 26, 283 (1956) (T. p. 301).*

[2] T. F. Platonova, A. D. Kuzovkov and P. S. Massagetov, J. Gen. Chem. 23, 880 (1953) (T. p. 921).*

[3] T. F. Platonova and A. D. Kuzovkov, J. Gen. Chem. 24, 2246 (1954) (T. p. 2215).*

[4] V. V. Kiselev and R. A. Konovalova, J. Gen. Chem. 22, 2233 (1952) (T. p. 2293).*

[5] M. O'Shaughnessy and W. Rodebush, J. Am. Chem. Soc. 62, 2906 (1940).

[6] G. H. Beaven, D. M. Hall, M. S. Lesslie and E. E. Turner, J. Chem. Soc. 1952, 854.

[7] H. Gilman, Organic Chemistry (New York, 1953), Vol. III.

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*T. p. = C. B. Translation pagination.

DISCUSSION

THE QUESTION OF THE COMPOSITION OF THE COPPER PYROPHOSPHATE BATH

E. A. Ukshe and A. I. Levin

Papers by I. L. Agafonov [1] and V. P. Vasilyev and K. B. Yatsimirsky [2], containing a number of remarks pertaining to our study [3], were published in the Discussion Section of the Journal of General Chemistry.

Since most of these remarks deserve serious answer, and since the question raised in the cited studies relative to the real state of the copper-pyrophosphate electrolyte is of considerable interest in practice, we consider it obligatory to discuss the critical remarks made by I. L. Agafonov, V. P. Vasilyev and K. B. Yatsimirsky.

We will begin with the study of V. P. Vasilyev and K. B. Yatsimirsky. These authors correctly note the error, assumed by us in calculating the instability constant of the complex $Cu(P_2O_7)_2^{6-}$. Actually, the experimental data presented in our paper on the potential of the copper electrode led to a value of $1.3 \cdot 10^{-11}$ for the constant, as had been indicated in one of our other studies [4], and not to a value of $0.5 \cdot 10^{-10}$ [3]. This difference is practically without effect on the subsequent results.

The second remark of V. P. Vasilyev and K. B. Yatsimirsky reduces to the fact that the equation

$$E - E^0_{Cu} = 0.03\left[\log K_1 + \log C^0_{Cu} - \log\left(C^0_{P_2O_7} - C^0_{Cu}\right)\right] \qquad (1)$$

is unsuitable for calculating the instability constant of the complex $Cu(P_2O_7)^{2-}$ in the case where $C^0_{P_2O_7} = C^0_{Cu}$, i. e. where the initial concentrations of pyrophosphate and copper are equal. This comment is trivial, for it is evident that in the indicated case equation (1) should be replaced by:

$$E - E^0_{Cu} = \frac{0.03}{2}\left[\log K_1 + \log C^0_{Cu}\right]. \qquad (2)$$

It is understood that we took this into consideration in our calculations of constant K_1 [3].

Further, V. P. Vasilyev and K. B. Yatsimirsky assert that our data on the instability constants of the complex $Cu(P_2O_7)^{2-}$ are unreliable for the reason that, based on our calculations, the complex $Cu(P_2O_7)^{2-}$ cannot compose more than 50% of the complex forms in solution, while in calculating the instability constants we assume that all of the free Cu^{2+} ions in solution are applied specifically to this complex, and not to $Cu(P_2O_7)_2^{6-}$.

At first glance such an assumption can actually appear to be without basis. However, it is easily confirmed by simple calculation. As a matter of fact for system No. 5, for example, (Table 1 [3]), we have $C^0_{Cu} = 0.03$, $C^0_{P_2O_7} = 0.05$ m, $E = +0.162$ V.

If it is assumed that for this system 50% of the copper enters into the composition of $Cu(P_2O_7)_2^{6-}$, and 50% into the composition of $Cu(P_2O_7)^{2-}$, we then obtain

$$2Cu^{2+} + 3P_2O_7^{4-} \rightleftarrows Cu(P_2O_7)^{2-} + Cu(P_2O_7)_2^{6-}, \qquad (3)$$

and therefore $[Cu(P_2O_7)^{2-}] \cong [Cu(P_2O_7)_2^{6-}] \simeq 0.5 \cdot C^0_{Cu} = 1.5 \cdot 10^{-2}$; $[P_2O_7^{4-}] \simeq C^0_{P_2O_7} - \frac{3}{2} C^0_{Cu} = 5 \cdot 10^{-3}$; while the reaction equilibrium constant is [3]:

$$K = K_1 K_2 = \frac{[Cu^{2+}]^2 [P_2O_7^{4-}]^3}{[Cu(P_2O_7)^{2-}][Cu(P_2O_7)_2^{6-}]} \approx \frac{[Cu^{2+}]\left(C^0_{P_2O_7} - \frac{3}{2} C^0_{Cu}\right)^3}{0.25 (C^0_{Cu})^3}. \quad (4)$$

when $K = 0.8 \cdot 10^{-17.2}$, and if $K_2 \cong 10^{-11}$, then $K_1 = 0.8 \cdot 10^{-6.2}$, which does not differ from the earlier obtained $K_1 = 10^{-6.2}$. A similar calculation for the remaining systems is even more complicated, since we do not know beforehand in which proportions the complexes $Cu(P_2O_7)^{2-}$ and $Cu(P_2O_7)_2^{6-}$ are formed, if their instability constants are not known. Incidentally, we will mention here an error by I. L. Agafonov, who postulates [1] that the solution to the last problem reduces to writing the equation for a reaction of the (3) type with the stoichiometric coefficients before the Cu^{2+} and $P_2O_7^{4-}$, determining their ratio $C^0_{Cu} : C^0_{P_2O_7}$. In treating this problem in our paper [3] we postulated that when $C^0_{Cu} : C^0_{P_2O_7} = 2/3$ it is possible for the copper to migrate completely into the $Cu(P_2O_7)_2^{6-}$ ion. As a matter of fact, with the indicated ratio the concentration ratio $[Cu(P_2O_7)_2^{6-}] : [Cu(P_2O_7)^{2-}]$ evidently becomes even less than 1.

However, here the bend, experimentally established in our study, on the electroconductivity-concentration curves, corresponding to $C^0_{P_2O_7} : C^0_{Cu} = 3/2$ becomes incomprehensible, although, contrary to the opinion of I. L. Agafonov [1], there is no reason to doubt the existence of such a bend. The analogous measurements of Rogers and Reynolds [5] also speak in support of its existence. As a result, an explanation of this effect is possible only after a more detailed study of the examined system has been made.

I. L. Agafonov further asserts that at a ratio $C^0_{P_2O_7} : C^0_{Cu} < 2$ a precipitate deposits in the solution only when the total copper concentration exceeds 10^{-4} M. This was not supported in our work, since the appearance of turbidity in dilute solutions ($C^0_{Cu} \leq 10^{-2}$ M) was observed only at $C^0_{P_2O_7} : C^0_{Cu}$ equal to 1.0-1.5, while according to the data of Rogers and Reynolds [9], a precipitate of $Cu_2P_2O_7$ deposits only at $C^0_{P_2O_7} : C^0_{Cu} = 0.5$.

It is also impossible to agree with the later statement of I. L. Agafonov that equilibrium is established in solution under the conditions $C^0_{P_2O_7} : C^0_{Cu} = 1$:

$$4CuSO_4 + 4Na_4P_2O_7 \rightleftarrows Na_6Cu(P_2O_7)_2 + Na_2Cu_3(P_2O_7)_2 + 4Na_2SO_4. \quad (5)$$

Any evidence in support of such a hypothesis is also absent in the earlier study of I. L. Agafonov, A. L. Agafonova and I. G. Shcherbakov [6]. The authors of the latter paper did not even attempt to experimentally determine the composition of the bottom phase under the conditions where a precipitate is actually formed, and instead invented reaction (5), probably from purely intuitive considerations.

Completely without basis is the statement made by I. L. Agafonov that ". . . at the concentrations, required in electroplating practice, the ionic composition of the solution is determined not as much by the excess $P_2O_7^{4-}$ ions, as by dilution of the solution or the formation of a precipitate with a deficiency of these ions . . .". Here I. L. Agafonov confuses the meaning of the terms "ionic composition of the solution" and "concentration of ions in solution". The concentration of "free" pyrophosphate specifically determines (at constant pH) the solution composition. The formation of a precipitate influences only the concentration of the ions in solution (also at pH = const).

Also we cannot agree with statements like: ". . . without changing the nature of the discharging (emphasis is provided by us) ions, it is impossible to obtain the solution concentrations indicated by the authors (i. e. E. A. Ukshe and A. I. Levin)". "By adding sodium citrate, the authors in this manner anticipated the deposition of a precipitate, in which connection the composition of the discharging ions evidently changed partially".

These statements of I. L. Agafonov contradict both experiment and basic theoretical considerations [7]. Although the additions of foreign complex-formers do dissolve the precipitates, capable of being formed in the anolyte, they are practically without effect on the cathode process. As is known, such additions (seignette salt, sodium citrate, ammonia) have found wide use in electroplating practice [8, 9]. On the other hand, the copper-pyrophosphate electrolyte, devoid of SO_4^{2-} ions, as is known, was proposed by A. I. Gershevich and L. V. Gamburg [10, 12] in 1940, and was studied in detail in the work of I. S. Titov, M. E. Yanitskaya and E. A. Prandetskaya [11], and not by I. G. Shcherbakov, as stated by I. L. Agafonov.

In conclusion we will mention that in the paper under discussion [3] our goal was not to make a complete study of the composition of the copper-pyrophosphate electrolyte, but instead we set ourselves a much more modest goal, namely, to elucidate to what extent the instability constants of the ions $Cu(P_2O_7)_2^{6-}$ and $Cu(P_2O_7)^{2-}$ differ from each other. The potentiometric study method used by us is in itself extremely approximate for a number of reasons, the chief of which are the following: 1) ignorance as to the activity coefficients of the ions (working with a constant ionic strength could not save the situation here, but would only make the experimental error constant); 2) ignorance as to the diffusion potentials, which can apparently attain extremely high values at the boundary of solutions of the type of $CuSO_4$–$Cu(P_2O_7)_2^{6-}$; the use of a salt bridge cannot guarantee their elimination; 3) the lack of precision for the standard electrode potential of copper, which is known only with an accuracy of a hundredth of a volt [13].

This approximate nature of the potentiometric method used in itself does not permit the expectation of obtaining "exact" results by its use. It is known that its accuracy fails to exceed a log K unit. On the other hand, the system $CuSO_4$–$Na_4P_2O_7$ is made very complicated by the formation of various precipitates or complexes of the type of $Cu(HP_2O_7)$ $(P_2O_7)^{5-}$ and $Cu(P_2O_7)OH^{3-}$. Up to now the influence of these impediments has not been studied sufficiently even for dilute solutions [14, 15]. It is natural that a further study of copper-pyrophosphate electrolytes is completely essential, and a discussion of the difficulties that arise here is of great interest.

LITERATURE CITED

[1] I. L. Agafonov, J. Gen. Chem. 25, 1231 (1955) (T. p. 1179).*

[2] V. P. Vasilyev and K. B. Yatsimirsky, J. Gen. Chem. 25, 1233 (1955) (T. p. 1181).*

[3] E. A. Ukshe and A. I. Levin, J. Gen. Chem. 24, 775 (1954) (T. p. 781).*

[4] E. A. Ukshe and A. I. Levin, J. Phys. Chem. 27, 1396 (1953).

[5] Rogers and Reynolds, J. Am. Chem. Soc. 71, 2081 (1949).

[6] I. L. Agafonov, A. L. Agafonova and I. G. Shcherbakov, J. Phys. Chem. 28, 147 (1954).

[7] A. I. Levin and E. A. Ukshe, J. Phys. Chem. 28, 1859 (1954).

[8] S. Senderoff, Metal Finishing 48, 59, 71 (1950).

[9] N. P. Fedotyev, editor, Handbook on Protective-Decorative Coatings (Moscow-Leningrad, 1951).

[10] A. I. Gershevich and L. V. Gamburg, Corrosion and Its Control (1940), 6, 46.

[11] I. S. Titov, M. E. Yanitskaya and E. A. Prandetskaya, Collected Transactions, Moscow Institute Light Metals and Gold (1947), 108.

[12] A. I. Gershevich, Thesis Reports at the 2nd All-Union Conference on Theoretical and Applied Electrochemistry (Kiev, 1948), p. 25.

[13] D. Bokris and L. Geringshou, Progr. Chem. 22, 246 (1951).

[14] Onstott and Laitinen, J. Am. Chem., Soc. 72, 4724 (1950).

[15] Eriksson, C. A. 1950, 3392.

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ERRATA TO ISSUES 1-5, 1956

The following mistakes which occurred in the original Russian were not corrected in the English translation:

Page	Line	Reads	Should read
1			
12	11, from bottom	(pH 7-7.)	(pH 7-7.5)
54	last line	$C_{11}H_{21}O_3F$	$C_{11}H_{20}O_3F$
264	3, from bottom	$C_{32}H_{28}O_4N_3Cl_6Pt$	$C_{32}H_{28}O_4N_2Cl_6Pt$
286	10, from top	$C_{16}H_{17}B_4SiP$	$C_6H_{17}O_4SiP$
1018	5, from bottom	m.p. 96°	b.p. 96°
1228	Caption to Figure 1	0.3 mol. %	0.3 wt. %
1230	Caption to Figure 3	0.3 mol. %	0.3 wt. %